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Final Report
for the period
November 1982 to
November 1984

Modification of Propellant Binder Network for Improvement of Mechanical Properties

December 1984

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FIELD	GROUP	SUB. GR.							
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The blending of long straight chain hydroxy-terminated prepolymers with branched shorter chain hydroxy-terminated prepolymers yields cured rubbers, whether containing solid fillers or not, that have large improvements in strain capability compared to short chain prepolymer rubbers. Also, the stress capability of the cured rubbers is improved compared to the long chain prepolymer rubbers. Polyethylene glycol 8000 (PEG 8000) was successfully blended with glycidyl azide polymer (GAP) and polydinitropropyl acrylate. Large equivalent weight lithium initiated, hydroxy-terminated polybutadiene improved the strain capability of R-45M cured rubbers. Pentanetriisocyanate greatly improved the tensile stress and strain for PEG 8000/polydinitropropyl acrylate binder, but did not improve the PEG 8000/GAP binder. These polymer blending and triisocyanate cross-linker techniques are applicable to curable solid propellant formulations.									
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Polydinitropropylacrylate, Tensile Properties.

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GLOSSARYAbbreviations

BDNPF/A	1:1 mixture of Bisdinitropropyl formal and Bisdinitropropyl acetal
DBU	1,8-Diazobicyclo [5.4.0]undec-7-ene
DEGDN	Diethyleneglycoldinitrate
Desmodur N-100	Polyfunctional aliphatic isocyanate from Mobay
FeAA	Ferric acetylacetone
GAP	Glycidyl azide polymer
GPC	Gel Permeation Chromatography
HDI	Hexamethylene diisocyanate
HMX	sym-Tetramethylene tetranitramine
HTPB	Hydroxy-terminated polybutadiene
L-2291A	Polyfunctional aliphatic isocyanate from Mobay
NP	Nitroplasticizer (BDNPF/A)
PBD	Polybutadiene
PCP	Polycaprolactone
PDNPA	Polydinitropropyl acrylate
PDMS	Polydimethyl siloxane
PEG	Polyethylene glycol
PHPBD	Phillip's polybutadiene
PTI	1,3,5-Pentane triisocyanate
R-45M	Polybutadiene from Arco

Symbols

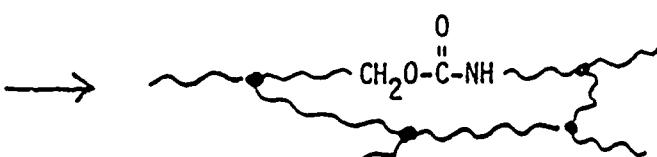
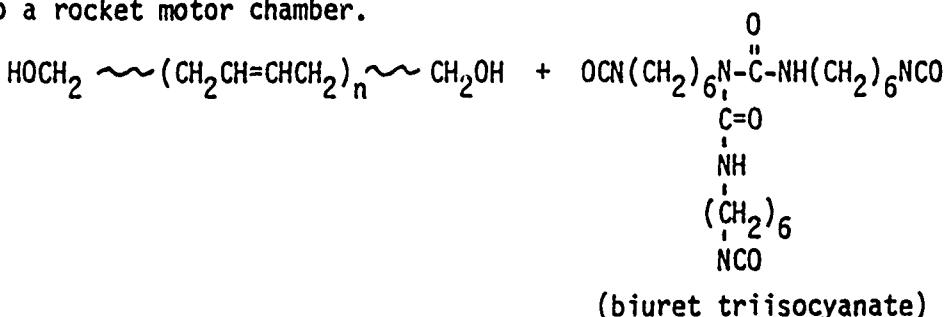
σ	Nominal stress
σ_r	Stress at rupture
ϵ	Percent elongation

Symbols (continued)

ϵ_r	Percent elongation at rupture
α	Extension ratio
E_0	Initial modulus
MPa	MegaPascal
M_n	Number average molecular weight
M_w	Weight average molecular weight
sk	Skeletal
Tg	Glass transition temperature
Tm	Melting temperature

1.0 INTRODUCTION

Rubbery materials find increasing application as binders for composites. Typical examples are solid propellants. The binder networks are formed by end-linking hydroxy-terminated prepolymers with di- and/or higher functional isocyanates. This reaction takes place after the liquid slurry has been cast into a rocket motor chamber.



The molecular weights of the prepolymer are usually 2000 to 4000, which ensures low enough viscosity so that pourable propellant slurries can be prepared.

A recent trend in solid propellant technology is the replacement of the traditional low-energy prepolymers such as polybutadienes, polyethers and polyesters, with "energetic" prepolymers in which nitro-, nitrato- or azido-groups are attached to the polymeric chain. Obviously, the number of skeletal atoms is far less for these energetic polymers than for the traditional polymers with the same molecular weight (Table I). Since the strain capabilities are primarily a function of the load-bearing skeletal atoms¹, with pendant energetic groups and semi-connected chains contributing little^{2,3}, the mechanical properties obtained with these polymers are notoriously poor. For example, the strain of binders formed from PDNPA with hydroxy equivalent weight of 3020 is comparable to that of PEG 600, which has equivalent weight of 294 (Table II). The approxi-

TABLE I
HYDROXY-TERMINATED PREPOLYMERS

Name	Chemical Structure/Type	Source	Mol. Wt.	OH-Eq.Wt.	Functionality	No. (wt.%) of Skeletal Atoms Between X-links
HTPB	$-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n(\text{CH}_2-\text{CH}(\text{CH}_2)_m\text{CH}_2$					
R-45M	Branched; 20 wt. % vinyl content	Arco	~3000	1100	~2.7	<70 (<76%)
PHPBD	14 wt. % vinyl content	Phillips	~9000	3600	~1.9	~500 (~78%)
PEG	$-(\text{CH}_2-\text{CH}_2-\text{O})_n$	Union Carbide	~600	294	~1.9	~40 (91%)
	"	"	~1000	500	~1.9	~70 (91%)
	"	"	~3500	1670	~1.9	~230 (91%)
	"	"	~9000	4300	~1.9	~550 (91%)
PCP	PCP^{J}	Union Carbide	~3000	1540	~2.0	~180 (77%)
0260	$-(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}-\text{O})_n$	Rocketdyne	~2300	1100	~2.0	~70 (40%)
GAP	$-(\text{CH}_2-\text{CH}-\text{O})_n$					
	CH_2-N_3					
PDNPA	$-(\text{CH}_2-\text{CH})_n$					
	$\text{C}=\text{O} \quad \text{NO}_2$					
	$\text{O}-\text{CH}_2-\text{C}-\text{CH}_3$					
	NO_2					
M-13	"	Synthesized	~9000	3200	~2.8	~55 (12%)
F-1	"	Synthesized	~4400	990	~4	~20 (12%)

TABLE-I
STRESS-STRAIN PROPERTIES OF MONOMODAL NETWORK OF SHORT CHAINS
(Polymer 29%, Plasticizers NP 13%, DEGDN 30% , HMX 2 μ , 28%)

<u>Polymer</u>	<u>$\overline{M_n}$</u>	<u>OH-Eq.Wt.</u>	<u>\overline{I}</u>	<u>Estimated skeletal atoms between x-link points</u>	<u>$66^0 C, 4.2 \times 10^{-4}$</u>	<u>σ_r (MPa)</u>	<u>ϵ_r (%)</u>	<u>E_0 (MPa)</u>	<u>m/s X-head speed</u>
PEG 600	600	294	~2	40		0.71	33	4.0	
PEG 1000	1000	500	~2	70		0.61	42	3.0	
GAP	2300	1100	~2	70		0.31	43	1.4	
PDNPA	9000	3020	~3	50		0.24	34	0.8	

mate numbers of skeletal atoms of PDNPA and PEG 600 are 50 and 40, respectively. The same comparison can be made between GAP and PEG 1000.

The objective of our project was to evaluate potential improvements in the stress/strain behavior of energetic propellant binders by bimodal network formation; i.e. by blending these energetic short chains with long chain prepolymers prior to cure into rubbers.

2.0 OBJECTIVE

The objective of this program is to determine the possibility of improving mechanical properties of energetic propellants via bimodal and/or multimodal binder network formation.

3.0 SUMMARY

One of the disadvantages of energetic prepolymers such as glycidylazidopolymers (GAP) or polydinitropropyl acrylates (PDNPA) is that the fraction of the polymeric chains bearing the load applied to the binder network is far less than that of conventional prepolymers such as polyethylene glycols (PEG) or polybutadienes (PBD). For example, only 40 weight % of GAP will participate in the strength and strain capabilities during deformation, in contrast to 91 weight % of PEG. Hence, these energetic prepolymers usually give poorer mechanical properties than PBD or PEG when formulated into elastomeric networks.

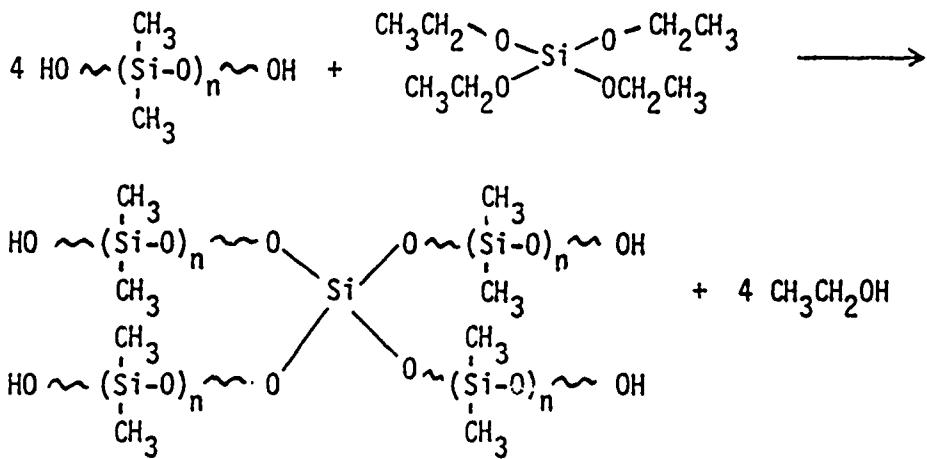
The objective of this project was to evaluate potential improvements in the stress/strain behavior of energetic propellant binders by bimodal network formation; i.e. by blending these energetic short chains with long chain prepolymers prior to cure into rubbers.

The advantage of the bimodal systems has been clearly demonstrated. For example, a PDNPA/PEG 8000 bimodal system at 35 weight % PEG 8000 shows an eight-fold increase in strain when compared with the monomodal PDNPA system. (The composite contained 50% TEGDN and 25% 2 μ HMX.) The improvements were examined

in terms of (1) polymer types and ratio of short/long chains; (2) strain rate; (3) type of crosslinker; (4) extent of cure reaction; (5) test temperature; (6) chain length of short chains; (7) chain length of long chains; and (8) solid filler content. The most important factors were types of the short chain prepolymers and the crosslinkers. Analysis of the results indicates that a significant improvement in the ultimate strain may be achieved if the rubber network undergoes an extensive nonaffine deformation.

4.0 RESULTS AND DISCUSSION

Recently, Mark⁴ prepared elastomeric bimodal networks by tetrafunctionally end-linking mixtures containing various proportions of relatively long and very short polydimethylsiloxane (PDMS) chains utilizing the following reaction:



The high molecular weight prepolymer had a number-average molecular weight (M_n) of 18,500 while the M_n of the short chains was 220, 660, or 1100 (Figure 1). Bimodal networks of PDMS prepared by blending short and long chains showed unique properties in which the strength increased rather significantly without the usual corresponding decrease of strain. Mark attributed this to intramolecular effects, specifically to non-Gaussian effects, arising from limited chain extensibility of the short chains. He observed that the shortest ($M_n = 220$) gave the most pronounced increase in the network rupture energy values, which are defined

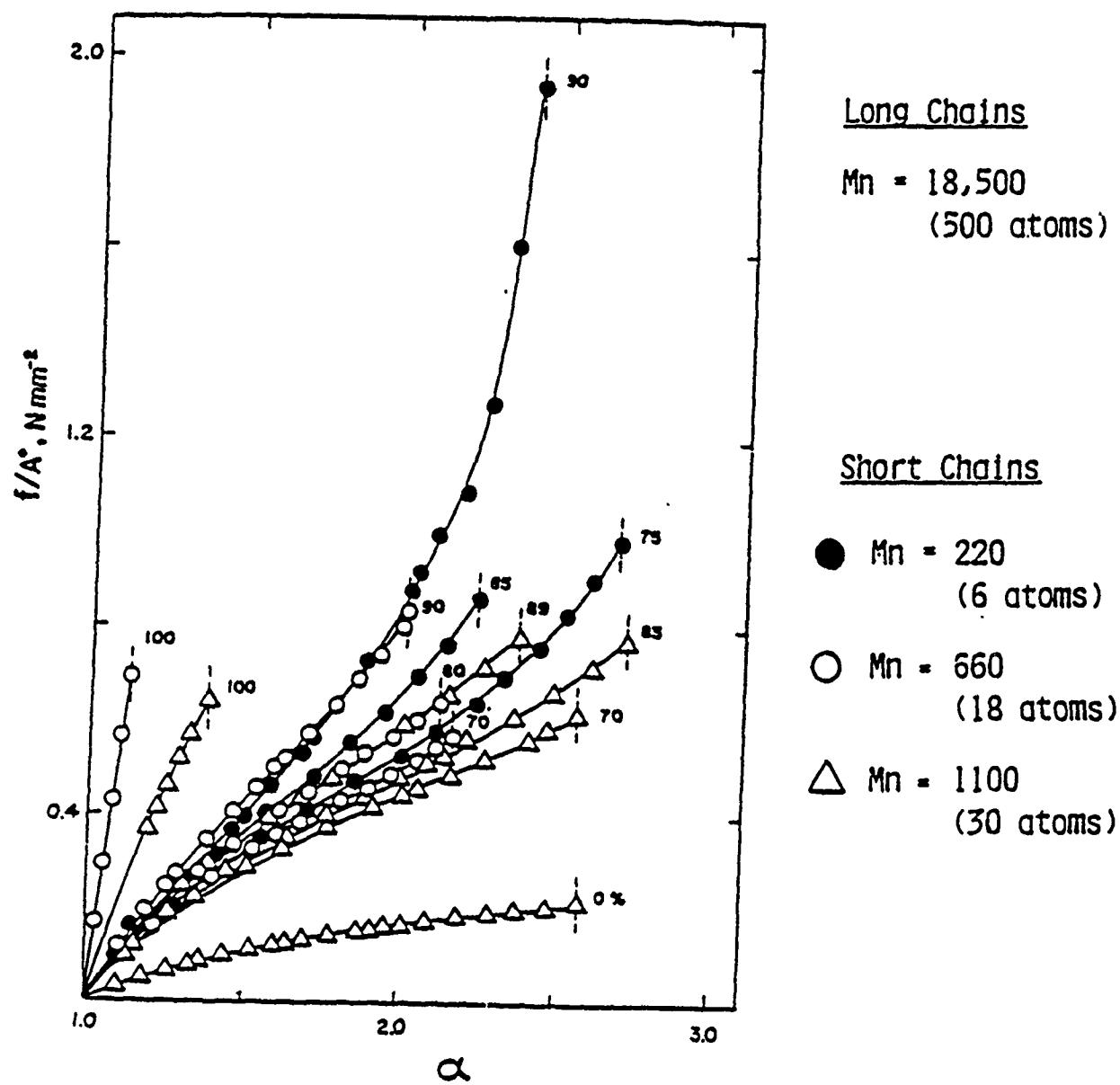


Figure 1. Typical plots of nominal stress against elongation, for tetrafunctional PDMS networks at 25°C (15). All but three networks are bimodal.

Number-average molecular weight of relatively long chains is $M_n = 18,500$ g/mol. Key for the networks where short chains had M_n (g/mol): Δ , 1,100; \circ , 660; \bullet , 220. Curves are labelled with the mol percent of short chains in the network. Area below curves represents the rupture energy per unit initial cross sectional area and per unit initial length.

as the area under the stress-strain curve. Mark's result negates the classical "weakest-link" theory⁵, which states that the shortest chains in the elastomeric network are the weakest, since they initiate rupture upon deformation.

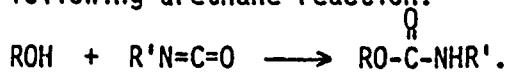
Mark tested his PDMS bimodal networks at room temperature. PDMS has very low T_g and low T_m and is close to an ideal elastomer. Furthermore, his experiments were performed near equilibrium conditions, where the maximum degree of nonaffine deformation is allowed. However, most of the rubbery binders for commercially practical composites, such as solid propellants, have polymeric chains with higher intra- and intermolecular forces and with higher rotational energy barriers. Their deformation behavior, therefore, would be more rate and temperature dependent than that of PDMS. Therefore, the composites with viscoelastic binders may not exhibit all the improvements shown by the bimodal elastomeric networks of PDMS. Presumably, the degree of improvement of composites containing bimodal rubber networks should depend on the intra- and intermolecular attractive forces of the rubber network, the rate of deformation, temperature, type and level of plasticizer and filler. The propellant binder properties were examined in terms of (1) polymer types and ratio of short and long chains; (2) strain rate; (3) type of crosslinker; (4) extent of cure reaction; (5) temperature; (6) chain length of short chains; (7) chain length of long chains; and (8) solid filler content.

4.1 Polymer Types and Ratio of Short/Long Chains

The rubber network systems examined were combinations of short/long prepolymer chains of the types shown below:

- A. polybutadiene (R-45M)/polybutadiene (PHPBD)
- B. polydinitropropyl acrylate (PDNPA)/ polyethylene glycol (PEG)
- C. glycidylazidopolymer (GAP)/ PEG
- D. PEG/PEG

Chemical structures, average hydroxyl equivalent weight and the weight % polymer used for load bearing chains in the rubber networks (% skeletal atoms) are shown in Table I for each of these polymers. All the rubber networks were created by the following urethane reaction:



4.1.1 Bimodal and Multimodal Networks of HTPB/HTPB

Polybutadienes have the least degree of intra- and intermolecular interactions among the prepolymers in Table I, and therefore are expected to be the closest in behavior to an ideal rubber and to PDMS.

R-45M was selected as the short-chain HTPB for this study. R-45M is highly branched, with an average functionality of 2.7, and does not have a well-defined polymer structure. The average interchain length between the OH groups is probably less than 70 skeletal atoms. The long chain HTPB was synthesized using BuLi as an initiator, and is therefore expected to be linear. The estimated average interchain length between OH groups is about 500 atoms. If these polymers are combined and reacted with an isocyanate having a functionality greater than 2 (N-100), the resulting network is bimodal; the use of the difunctional hexamethylene diisocyanate (HDI) produces a multimodal network, as depicted in Figure 2.

Desmodur N-100 from Mobay Chemical Corp. was analyzed by GPC, using n-butyliisocyanate and HDI as references. It was also treated with a ten times excess of 1-octanol. GPC peaks of N-100 shown in Figure 3 and the analysis of molecular weight in Figure 4 indicate that the sample contains negligible HDI, but contains mainly biuret triisocyanate (HDI-trimer) and biuret tetraisocyanate (HDI-tetramer) along with higher oligomers. The similar peak pattern for both the isocyanate and its urethane derivative indicates that the trimer contains 3 isocyanate groups, the tetramer contains four isocyanate groups and so on.

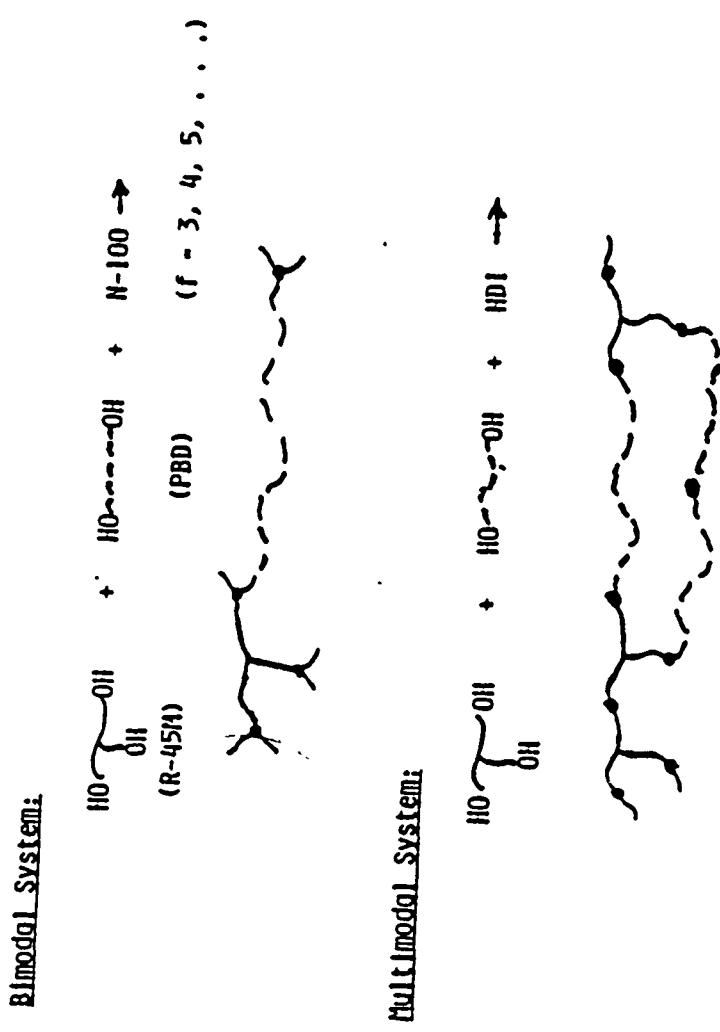


Figure 2. Hydroxy-Terminated Polybutadiene System

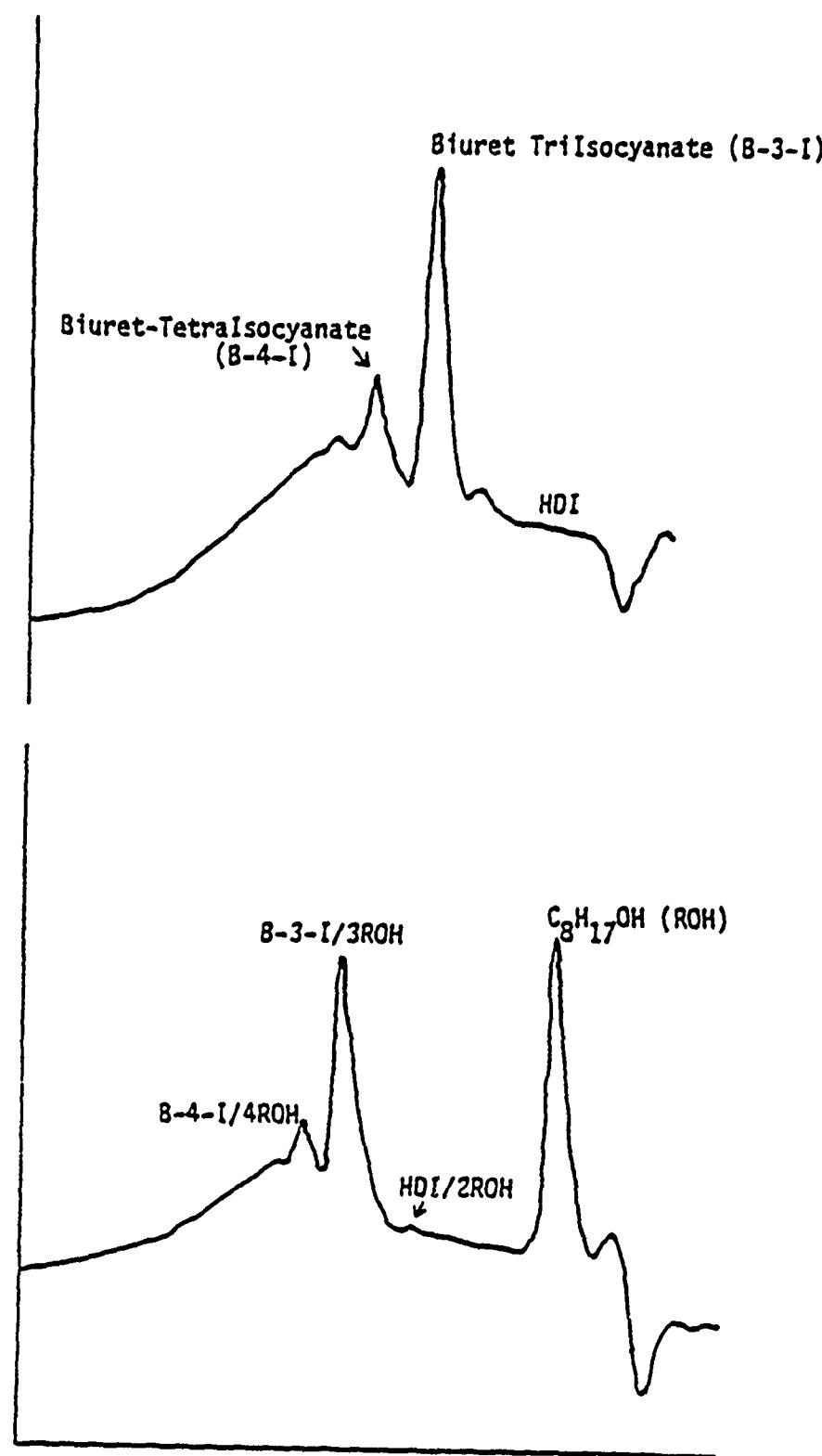


Figure 3. GPC Analysis of N-100 and Its n-Octanol Derivative

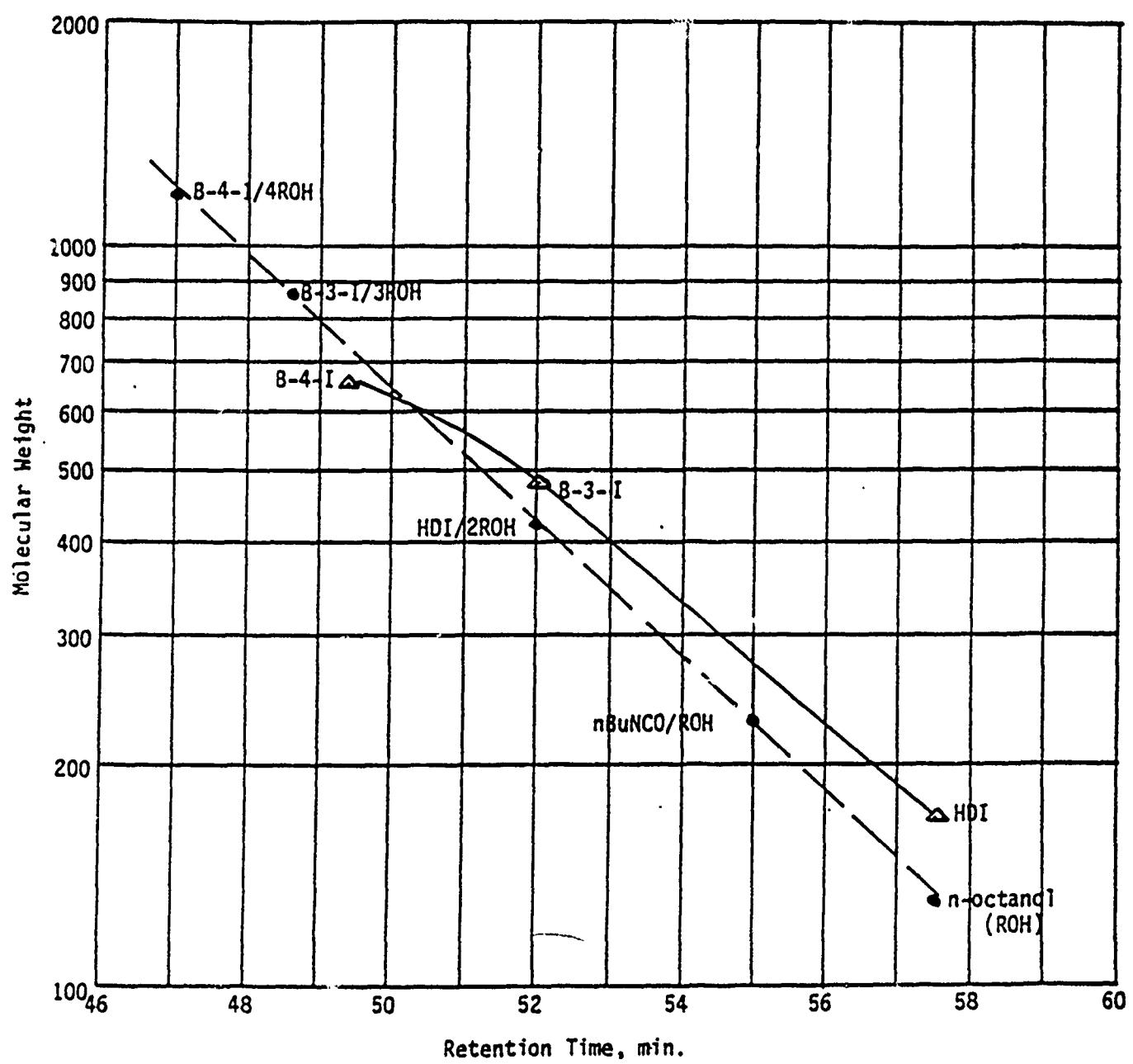


Figure 4. Molecular Weight Determination by GPC

Bimodal and multimodal networks of polybutadienes were prepared using N-100 and HDI as curatives. The bimodal system with 50/50 weight ratio shows an improvement in the ultimate stress/strain properties such that the strain capability is higher than that of the monomodal short chain system (R-45M) and the ultimate strength is greater compared to the monomodal long chain system (Table III). Multimodal systems in Table IV show improvements in both stress and strain properties over those of R-45M alone. These tensile tests were done under dynamic conditions at a strain rate of 4.2×10^{-4} m/s, in contrast to Mark's experiments under near equilibrium conditions.

4.1.2 Bimodal Networks of PDNPA/PEG, GAP/PEG, PEG/PEG at Different Compositions

Most of the polar prepolymers such as PDNPA and PEG are solids at room temperature, and therefore must be plasticized. Highly plasticized binders become very soft and often are weak to handle, and therefore have to be reinforced with solids to attain manageable strength. These plasticized samples had transition temperatures (softening points) below 0°C provided the weight fraction of PEG 8000 was less than 1/2 of the total polymer (Table V). These prepolymers were reacted with isocyanates having functionality greater than 3.0. Hence, the resulting networks have the same interchain length as the number of skeletal atoms between the hydroxyl groups of the prepolymers. Stress/strain data were obtained at 66°C in order to minimize the effect of crystallization of PEG 8000,

Ultimate stress/strain properties of plasticized and filled PDNPA (M-13)/PEG 8000 and GAP/PEG 8000 bimodal systems at 66°C are plotted against the weight % PEG 8000 (Figures 5 and 6). At 66°C , both ultimate stress and % elongation increase steadily with the weight % PEG 8000, although the initial modulus decreases due to lower crosslink density. However, the extent of improvement appears to be strongly dependent on the type of polymer systems. The PEG/PEG

TABLE III
"BIMODAL" POLYBUTADIENE SYSTEM
(16.7% IDP, N-100/OH = 1.1, FeAA Catalyst)

R-45M/PHPBD (Wt. Ratio)	Cross-Head Speed 4.2×10^{-4} m/s; 25°C		
	σ_r , MPa	ϵ_r , %	E_o , MPa
100/0	1.0	50	2.8
50/50	0.97	100	1.8
0/100	0.69	140	1.1

TABLE IV
"MULTIMODAL" POLYBUTADIENE SYSTEM
(16.7% IDP, HDI/OH = 1.1, FeAA Catalyst)

R-45M/PHPBD (Wt. Ratio)	Crosshead Speed 4.2×10^{-4} m/s; 25°C		
	σ_r , MPa	ϵ_r , %	E_o , MPa
100/0	0.76	70	1.9
80/20	0.83	130	1.6
70/30	0.97	160	1.7
60/40	0.90	180	1.7

TABLE V

APPROXIMATE TRANSITION TEMPERATURES OF BIMODA POLYMER/PEG 8000 RUBBERS
 (29% Polymer, 30% DEGDN, 13% NP, 28% HMX)

wt. % PEG 8000 of Polymer Blend	Transition Temperatures, $^{\circ}\text{C}$		
	PEG 1000/PEG 8000	GAP/PEG 8000	PDNPA/PEG 8000
0	-55	-55	-55
9	-55	-55	-55
20	-55	-55	-55
30	-55, -5	-45	-55, -15
50	-55, +5	-45, -15	-45, 0
65	+15	+10	+15
100	+28	+23	+28

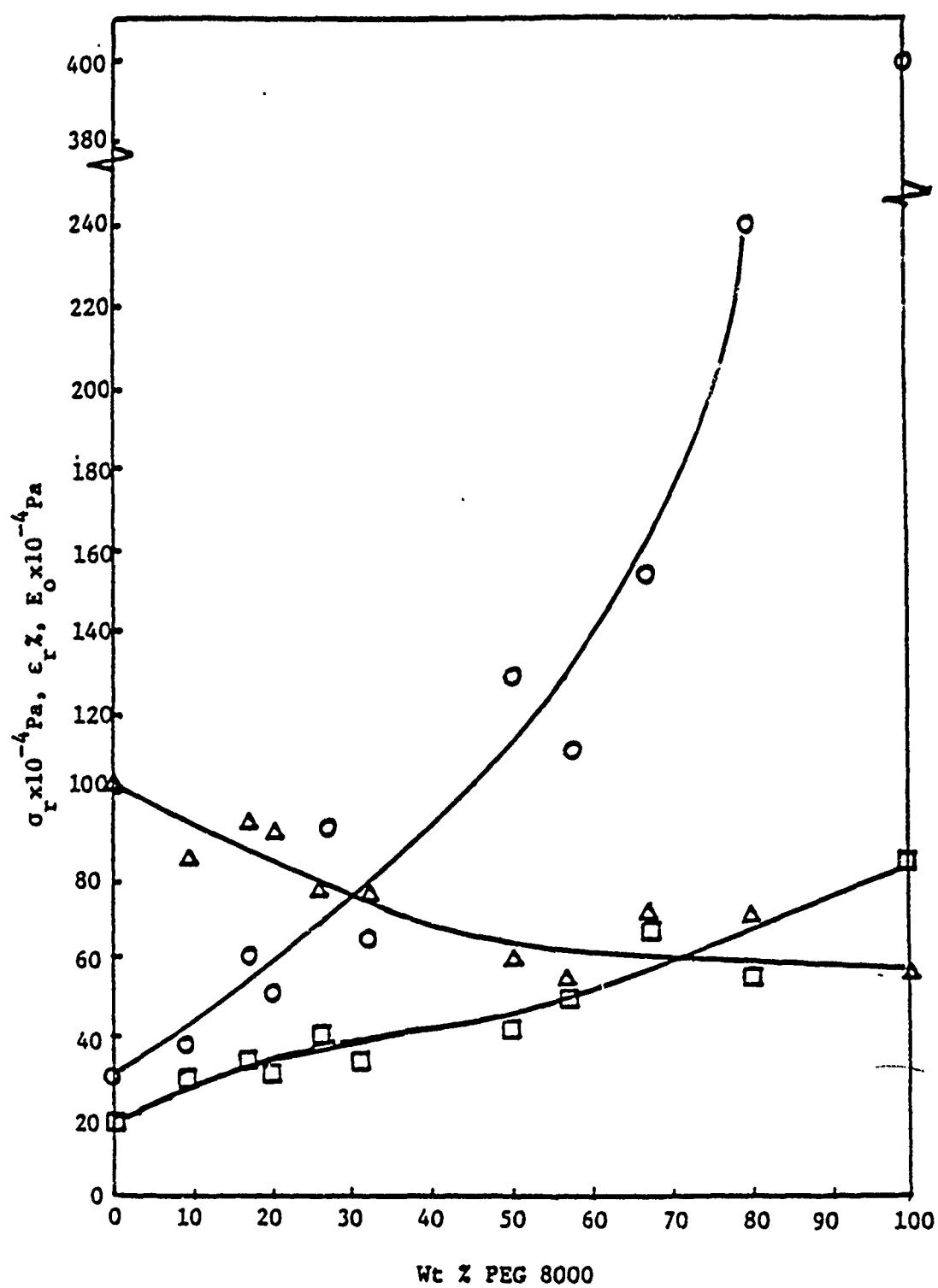


Figure 5. Ultimate Stress/Strain Properties of PDNPA (M-13)/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 66°C; Strain Rate 4.2 $\times 10^{-4}$ m/s; $\square \sigma_r$; $\circ \epsilon_r$; ΔE_0

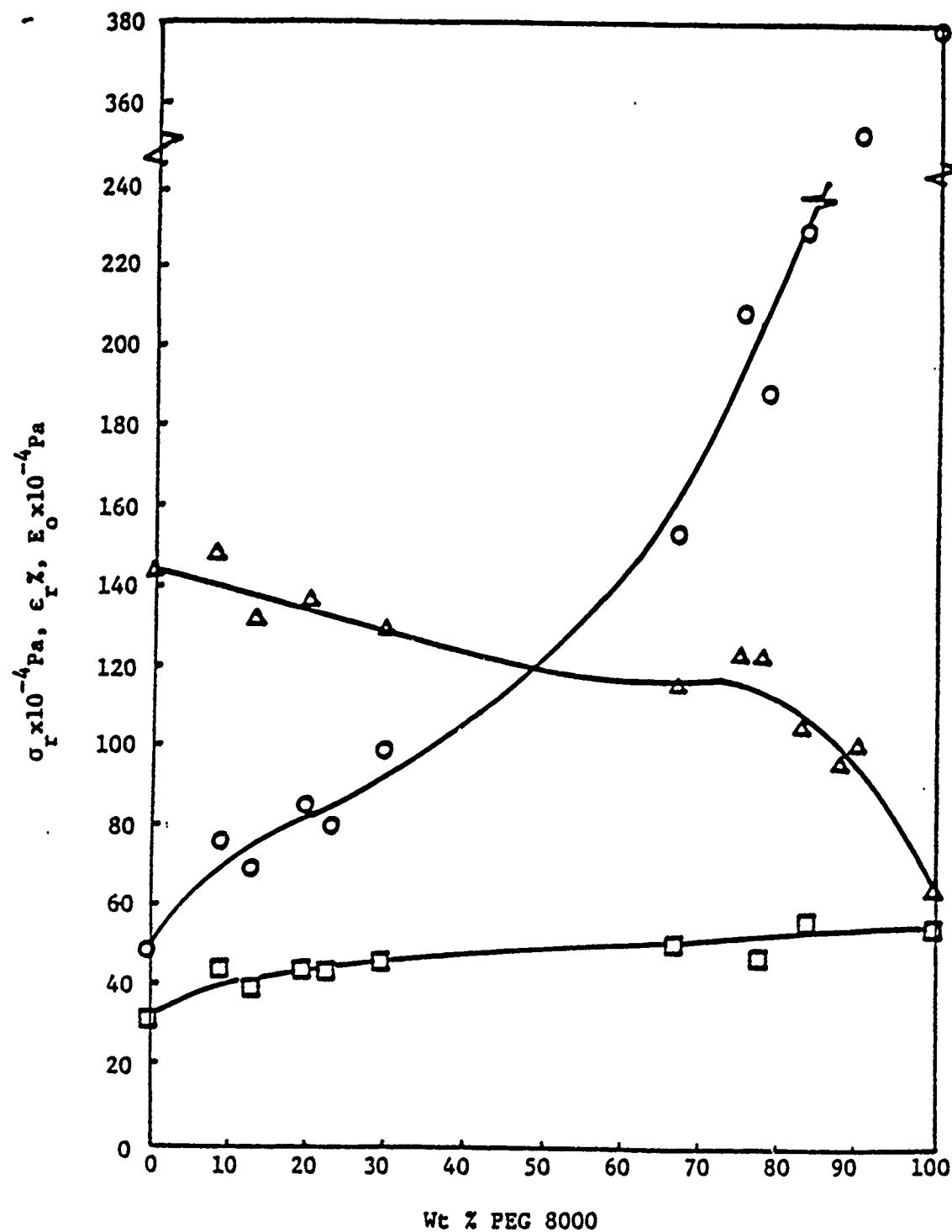


Figure 6. Ultimate Stress/Strain Properties of GAP/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 66°C; Strain Rate $4.2 \times 10^{-4} \text{ m/s}$; $\square \sigma_r$; $\circ \epsilon_r$; $\triangle E_0$

systems show negligible improvement in comparison with PDNPA/PEG and GAP/PEG systems when the weight % of PEG 8000 is less than one-half of the total polymer, as shown in Figures 7 and 8.

The bimodal systems of short chains having comparable chain lengths between the crosslinks are compared at various mole % PEG 8000. Monomodal systems of these short chains with about the same interchain length have about the same elongation at rupture, indicating that the strain capability is mainly a function of the number of load-bearing skeletal atoms between the crosslink points (Table II). However, the % elongation at rupture of the bimodal networks of PDNPA/PEG 8000 and GAP/PEG 8000 nearly triples when 15 mole % of PEG 8000 is incorporated, whereas that of the PEG/PEG system increases at most 1.5 times (Figure 9).

The improvements of bimodal systems over short chain monomodal systems may be explained by (1) nonaffine deformation of bimodal systems, i.e. lack of extension of the short chains is compensated by the neighboring long chains, and/or (2) long chains acting as inhibitor of the growth or rupture nuclei. The differences in improvement in these solid-filled bimodal systems at the same mole % of PEG 8000 (Figure 9) indicates that the improvement is mainly due to nonaffine deformation. The degree of nonaffine deformation in these bimodal systems may be influenced by (1) different degree of H-bonding (at the crosslink points), and (2) additional plasticization by the side-groups in GAP and PDNPA. In PEG/PEG systems the acidic hydrogen atoms of the urethane groups and urea groups (from N-100) would undergo extensive intra- and intermolecular H-bonding with PEG, whereas in the PDNPA/PEG and GAP/PEG systems the H-bonding is substantially reduced by the interference of the dangling side-groups and the reduced number of ether-oxygen atoms. Ether-oxygen atoms are known to form fairly strong H-bonds. Furthermore, intramolecular H-bonding to form a 7-membered ring

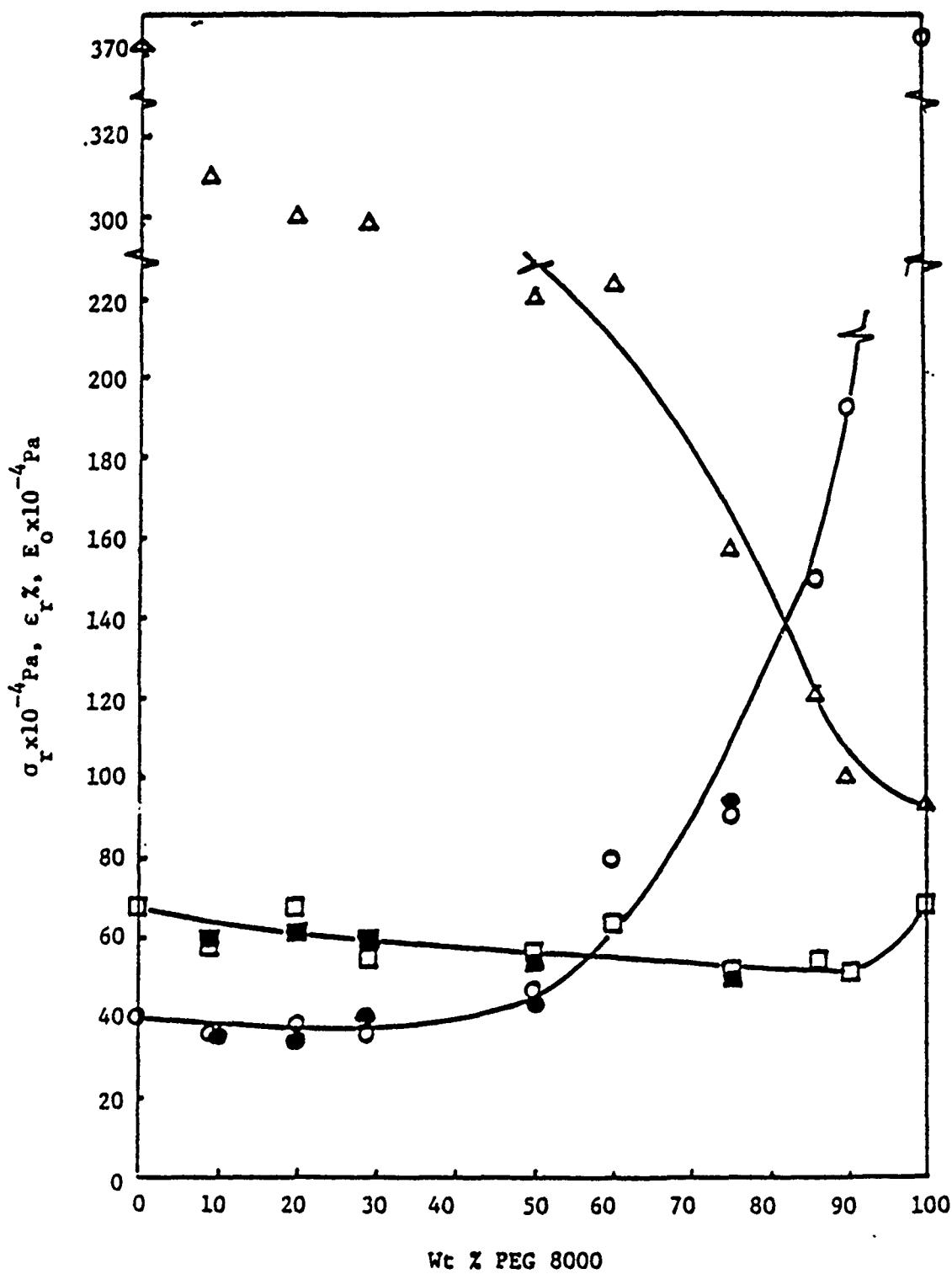


Figure 7. Ultimate Stress/Strain Properties of PEG 1000/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 66°C; Strain Rate: Open symbols are at $4.2 \times 10^{-4} \text{ m/s}$; and Filled symbols are at $4.2 \times 10^{-5} \text{ m/s}$; $\square \sigma_r$, $\circ \epsilon_r$, $\triangle E_0$

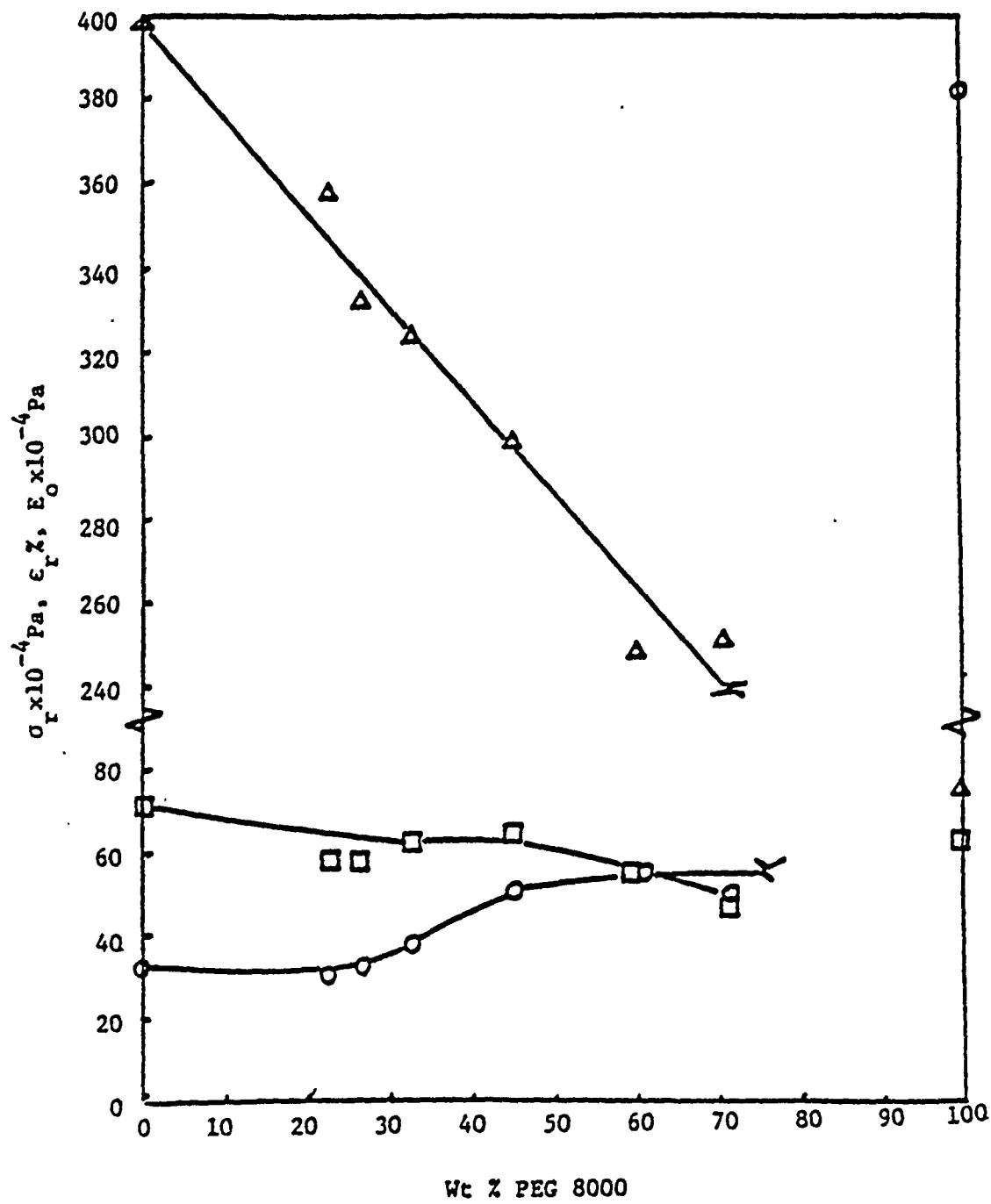


Figure 8. Ultimate Stress/Strain Properties of PEG 600/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 66°C, Strain Rate 4.2×10^{-4} m/s; $\square \sigma_r$, $\circ \epsilon_r$, ΔE_o

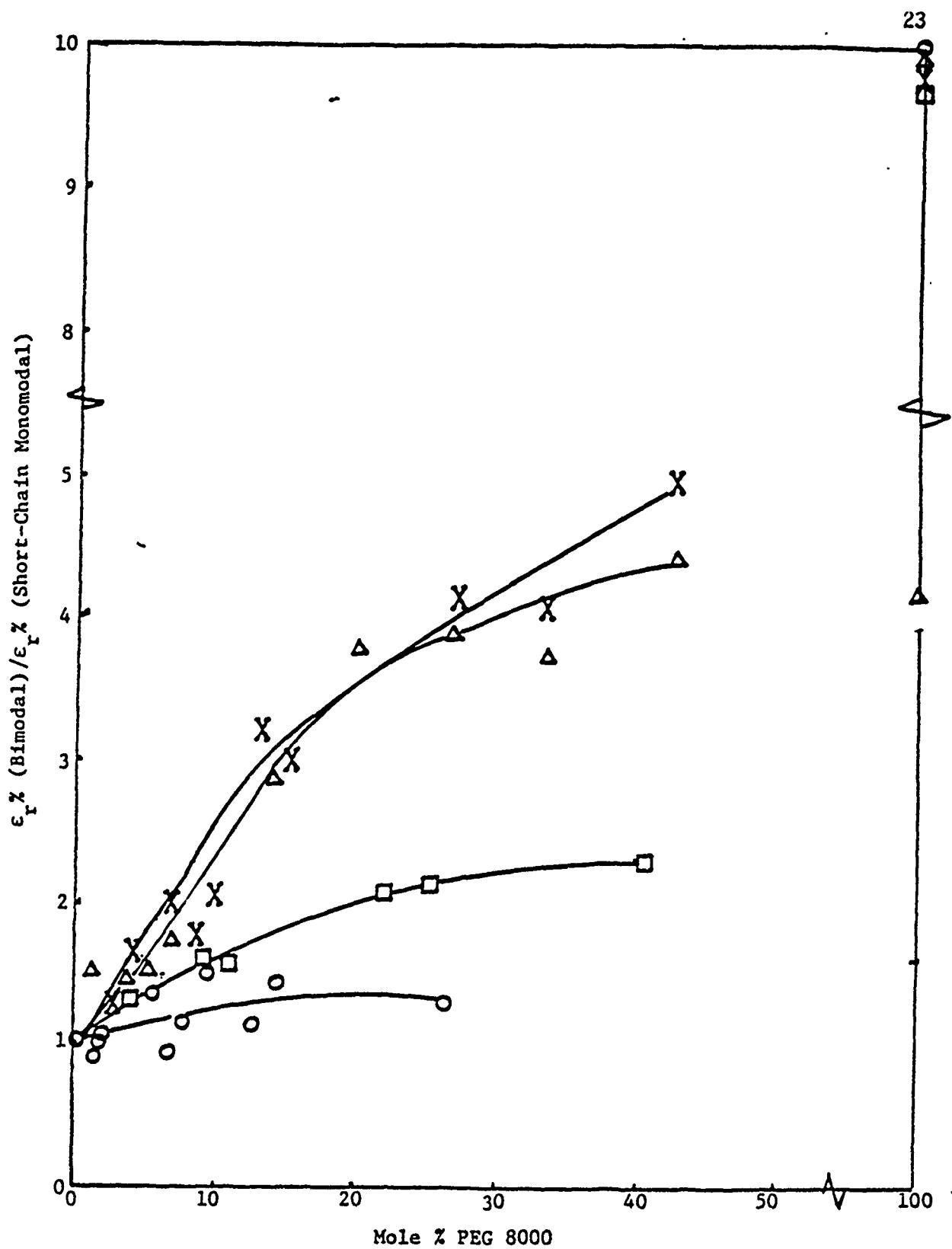
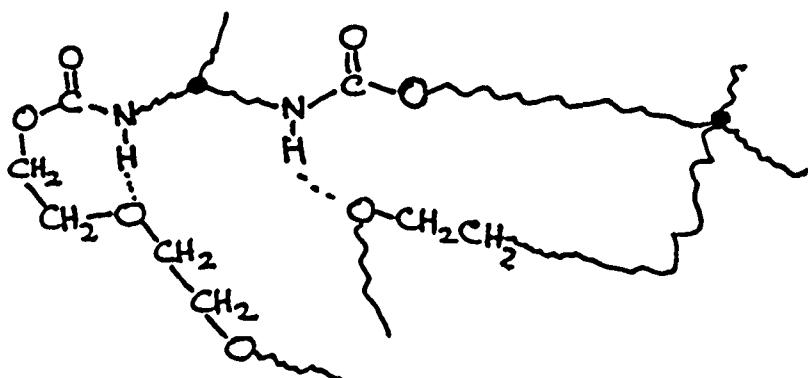


Figure 9. Improvement of Ultimate Strain Properties of Various Polymer/PEG 8000 Bimodal Systems vs Mole % PEG 8000 at 66°C; Strain Rate 4.2×10^{-4} m/s; \circ PEG 600 (40 sk. atoms), \square PEG 1000 (70 sk. atoms), \triangle GAP (70 sk. atoms), \times PDNPA (50 sk. atoms)

as shown below (short range interaction) is usually independent of the plasticizer content, and this type of intramolecular force may play a significant role in the PEG/PEG systems.



The H-bonds would then restrict the mobility of the polymeric chains, especially that of crosslink points, during the deformation of the network, and thus minimize the degree of nonaffine deformation. If so, the bimodal PEG/PEG systems should have ultimate properties similar to those of short chain monomodal PEG systems ("weakest-link" theory). On the other hand, it can be argued that the PDNPA/PEG and GAP/PEG bimodal systems give an additional free volume effect due to their side chains. These hypotheses are tested in the subsequent sections.

4.2 Effect of Strain Rate

The lack of significant change in the ultimate properties of both GAP/PEG and PEG/PEG systems when changing the strain rates as much as tenfold (Figure 10) indicates that the difference between the PEG/PEG vs. GAP/PEG or PDNPA/PEG systems is not mainly due to the difference in the degree of plasticization, i.e. free volume effect. It appears that once these polymers are sufficiently plasticized to create enough free volume to make the system reasonably flexible, additional decrease of viscosity does not significantly increase the extent of nonaffine deformation.

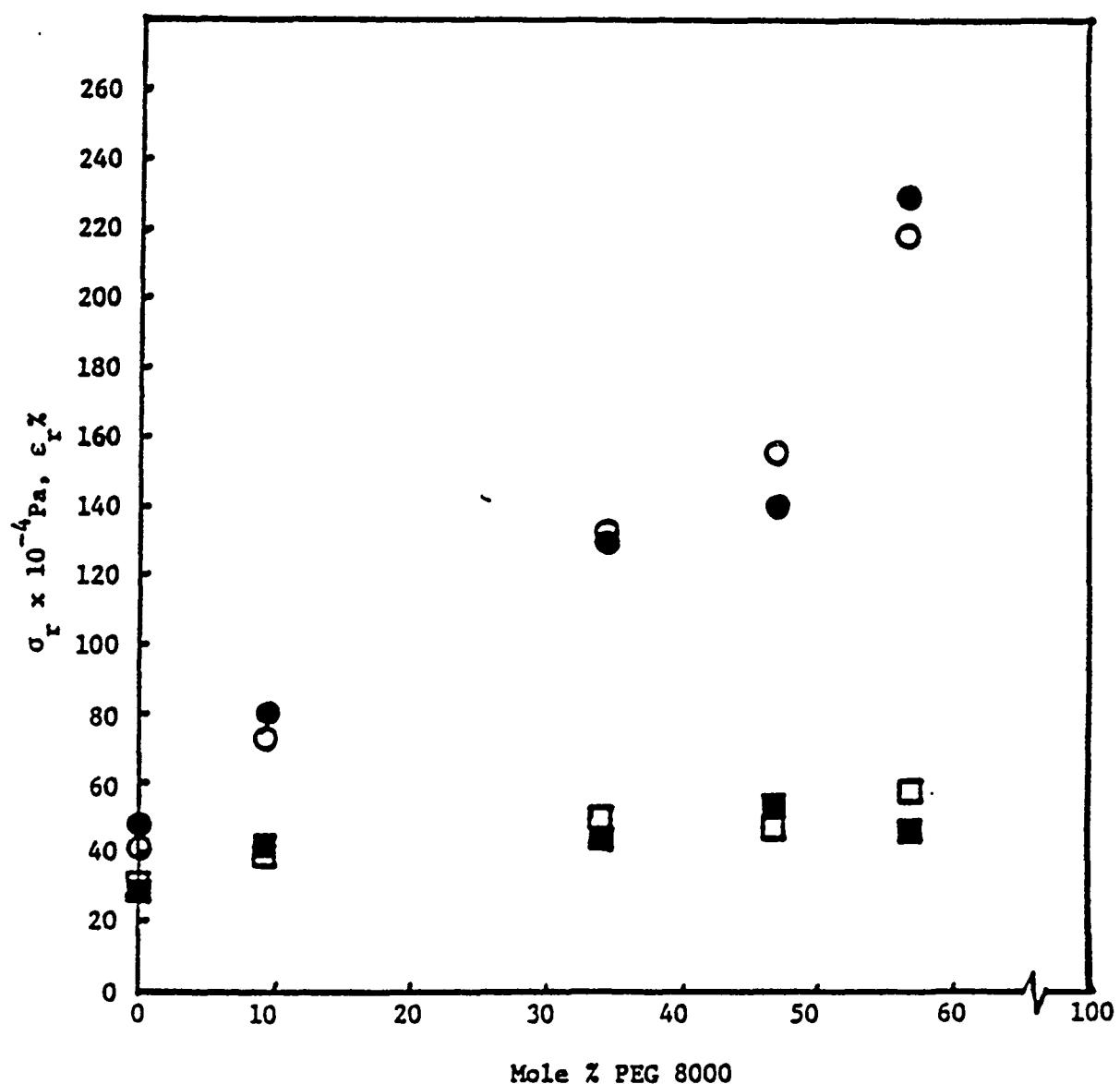
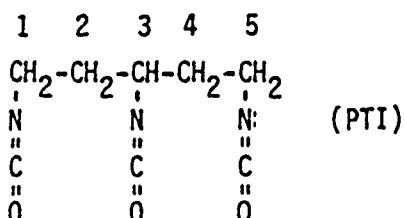


Figure 10. Effect of Strain Rate on Ultimate Properties of GAP/PEG 8000 Bimodal Systems at Different Mole % PEG 8000; Strain Rate: Open Symbols are at 4.2×10^{-4} m/s; and Filled Symbols are at 4.2×10^{-5} m/s; $\square \sigma_r$, $\bigcirc \epsilon_r$; 66°C

4.3 Effect of Crosslinker

All the previous rubber networks were prepared using Desmodur N-100 from Mobay Chemical Company as the crosslinker. A GPC analysis of N-100 (Figure 11) indicates that the sample contains approximately 26% biuret triisocyanate with functionality of three (fraction B), and the rest consists mainly of isocyanates with higher functionality. This percentage is an approximate value since the refractive index of each fraction is not known, and the fraction B may be a mixture of di- and tri-functional isocyanates. Possible structures and functionalities of the compounds in fractions A,B,C and D are listed in Table VI. A more recently acquired aliphatic "triisocyanate" from Mobay, L-2291A, contains a larger portion (47%) of fraction B and a smaller amount of higher functional isocyanates than N-100 (Table VII).

Crosslinkers which are less polar, with no H-bonding groups such as ureas, and which are trifunctional rather than tetra- or higher functional, would allow more extensive nonaffine deformation at a given strain rate and thus improve the ultimate properties further. Such a compound, 1,3,5-pantanetriisocyanate, has been synthesized.



The structure indicates that two isocyanates of PTI would undergo urethane reaction at a rate comparable to those of N-100 and L-2291A, but the 3-substituted isocyanate at a lower rate. The IR spectra of the aliphatic isocyanates, HDI, PTI, L-2291A and N-100 show that HDI and PTI have low urea concentration (urea N-H stretching at 3250 cm^{-1} and urea-C=O stretching at 1700 cm^{-1}) whereas N-100 and L-2291A have significant amounts of urea (Figure 12).

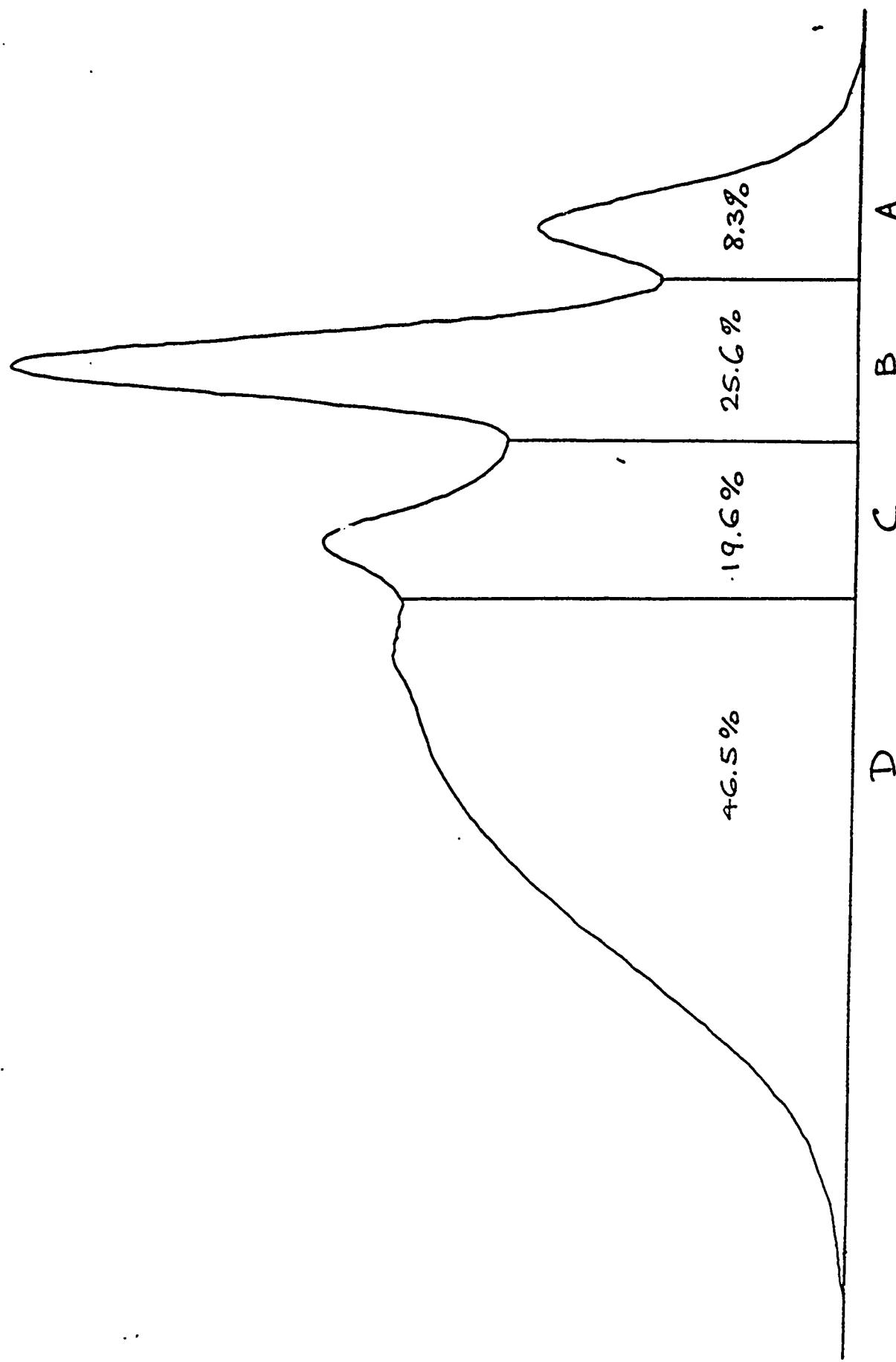


Figure 11. GPC Scan: Area Ratio of Different Components in N-100
(RI detector, THF solvent)

TABLE VI

ANALYSIS OF N-100 AND L-2291A: POSSIBLE
STRUCTURES AND FUNCTIONALITIES

	<u>Structure</u>	<u>Function- ality</u>
A	$\text{OCN}(\text{CH}_2)_6\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$	2
B	$\text{OCN}(\text{CH}_2)_6\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$	2
	$\text{OCN}(\text{CH}_2)_6\text{NH}-\overset{\text{O}}{\underset{\text{C=O}}{\text{C}}}-\text{N}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$ NH $(\text{CH}_2)_6$ NCO	3
C	$\text{OCN}(\text{CH}_2)_6\left\{\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\right\}_2\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$	2
	$\text{OCN}(\text{CH}_2)_6\text{NH}-\overset{\text{O}}{\underset{\text{C=O}}{\text{C}}}-\text{N}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$ NH $(\text{CH}_2)_6$ NCO	3
	$\text{OCN}(\text{CH}_2)_6\text{N}-\overset{\text{O}}{\underset{\text{C=O}}{\text{C}}}-\text{N}-\overset{\text{O}}{\underset{\text{C=O}}{\text{C}}}-\text{NH}(\text{CH}_2)_6\text{NCO}$ NH $(\text{CH}_2)_6$ NCO (sterically not favorable)	4

	<u>Structure</u>	<u>Functionality</u>
D	$\text{OCN}(\text{CH}_2)_6 \left[\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6 \right]_3 \text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6 \text{NCO}$	2
	$\text{OCN}(\text{CH}_2)_6 \left[\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{NH}(\text{CH}_2)_6 \right]_2 \text{N}-\overset{\text{O}}{\underset{\text{C}=\text{O}}{\text{C}}}-\text{NH}(\text{CH}_2)_6 \text{NCO}$ NH $(\text{CH}_2)_6$ NCO	3
	$\text{OCN}(\text{CH}_2)_6-\overset{\text{O}}{\underset{\text{C}=\text{O}}{\text{C}}}-\text{NH}-(\text{CH}_2)_6-\overset{\text{O}}{\underset{\text{C}=\text{O}}{\text{C}}}-\text{NH}(\text{CH}_2)_6 \text{NCO}$ NH $(\text{CH}_2)_6$ NCO	4
	$\text{OCN}(\text{CH}_2)_6-\overset{\text{O}}{\underset{\text{C}=\text{O}}{\text{C}}}-\text{N}(\text{CH}_2)_6 \text{NCO}$ HN $(\text{CH}_2)_6$ NCO	5 (sterically very unfavorable)

TABLE VII

PEAK RATIO OF DIFFERENT ISOCYANATES AND THEIR DERIVATIVES

<u>Fraction</u>	<u>L-2291 A</u>	<u>N-100</u>	
A	6.0%	8.3	Isocyanates
B	47.4	25.3	
C	20.9	19.6	
D	25.5	46.5	
A	2.3	1.9	N-Octanol Urethane Derivatives
B	61.4	44.5	
C	17.5	22.7	
D	18.6	30.7	

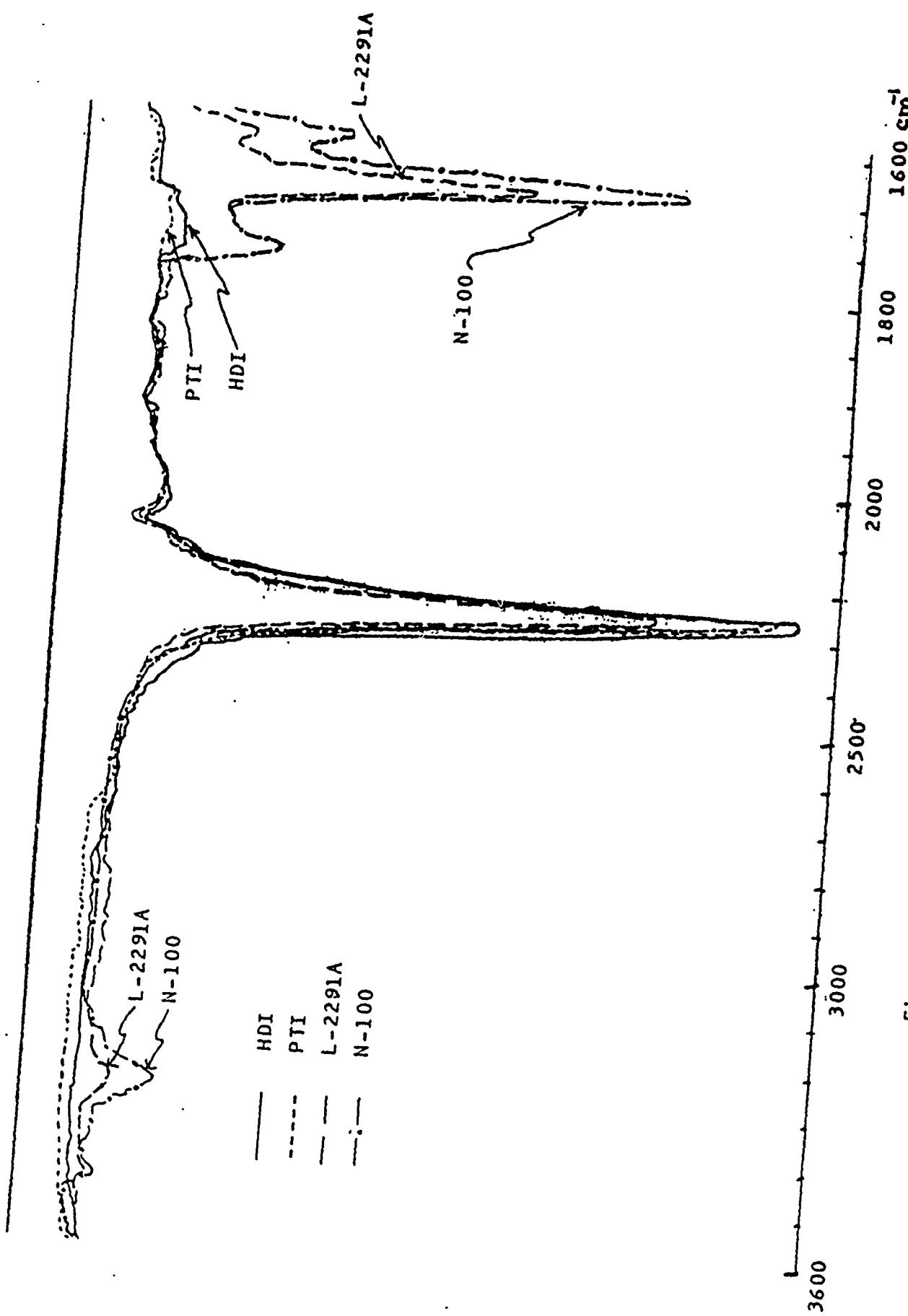


Figure 12. IR Spectra of Various Isocyanates

PDNPA having OH-functionality of approximately four was synthesized. The polymerization conditions were such that each polymer chain contains two or three primary hydroxyl groups and one or two secondary hydroxyl groups.

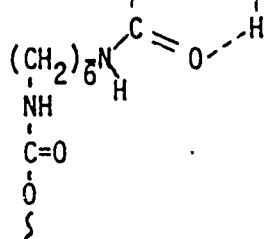
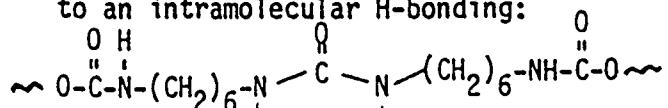
Characterization: OH-equivalent wt. = 1020 ±20

$$\text{Molecular wt. } \frac{M_n}{M_w} = 4400$$

Number of skeletal atoms between OH groups = 20

Solid filled and plasticized binders of PDNPA/PEG 8000 bimodal systems were prepared using PTI, L-2291A and N-100. Two different composites using equivalent ratios of NCO to OH at 1.1 and 1.2 were prepared. Stress/strain properties of minibones at a strain rate of 4.2×10^{-4} m/s at 66°C are tabulated in Tables VIII and IX. The effect of variation of the crosslinkers on the ultimate properties of monomodal short chain PDNPA is not significant. In fact, the strain is about the same for PTI, L-2291A and N-100. However, the properties of bimodal PEG 8000/PDNPA systems are strongly influenced by the type of crosslinker. The differences in the improvement of strain of the bimodal network systems over those of monomodal PDNPA systems are dramatic when PTI, L-2291A and N-100 are compared (Figures 13 and 14). PTI is far superior to L-2291A, which in turn is superior to N-100. The use of L-2291A or N-100 is expected to create relatively rigid crosslink points in the binder because

- (1) most of the compounds in the samples are substituted ureas, as demonstrated in the IR spectra (figure 12);
- (2) the isocyanates of fractions C and D have average functionalities greater than 3; and
- (3) the resulting crosslink point may have a 6-membered ring structure due to isocyanate self-coupling.



(Crosslink point when biuret triisocyanate is used.)

TABLE VIII
STRESS/STRAIN PROPERTIES* OF BIMODAL PEG 8000/PDNPA BIMODAL SYSTEM
(50% TEGDN; 20% 2μ HMX; NCO/OH = 1.1)

	<u>% PEG in PEG 8000/PDNPA Bimodal Network</u>								
	<u>0% PEG</u>			<u>35% PEG</u>			<u>45% PEG</u>		
	σ_r (MPa)	ϵ_r (%)	E_0 (MPa)	σ_r (MPa)	ϵ_r (%)	E_0 (MPa)	σ_r (MPa)	ϵ_r (%)	E_0 (MPa)
PTI	0.17	8.8	1.97	0.41	72.5	0.68	0.70	92.5	0.88
L-2291A	0.19	8.3	2.38	-	-	-	0.25	36.2	0.82
N-100	0.18	9	2.14	0.25	23.6	1.25	0.33	37.9	1.10

* Mini-bones; strain rate 4.2×10^{-4} m/s at 66°C.

TABLE IX
STRESS/STRAIN PROPERTIES* OF BIMODAL PEG 8000/PDNPA BIMODAL SYSTEM
(50% TEGDN; 25% μ HMX; NCO/OH = 1.2)

	<u>% PEG in PEG 8000/PDNPA Bimodal System</u>					
	<u>0% PEG</u>			<u>40% PEG</u>		
	σ_r (MPa)	ϵ_r (%)	E_0 (MPa)	σ_r (MPa)	ϵ_r (%)	E_0 (MPa)
PTI	0.09	7	1.45	0.72	96	0.70
N-100	0.17	8	2.12	0.41	40	1.28

* Mini-bones; strain rate 4.2×10^{-4} m/s at 66°C.

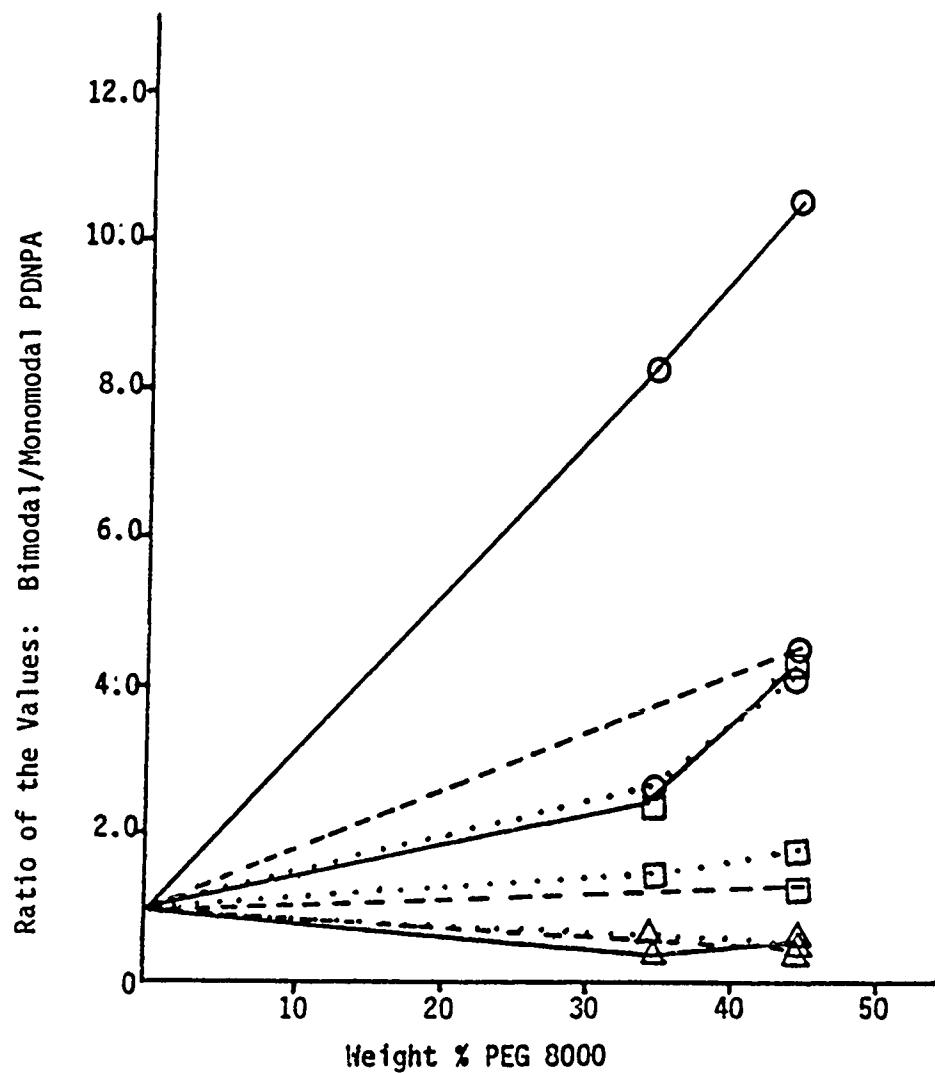


Figure 13. Reduced Stress/Strain Properties of PEG 8000/PDNPA Bimodal Systems vs. Weight % PEG 8000 at 66°C:
 (50% TEGDN; 20% 2 μ HMX; NCO/OH Equivalent ratio = 1.1)
 Strain Rate 4.2×10^{-4} m/s; $\square \sigma$; $\circ \epsilon$; $\triangle E_0$;
 — PTI; - - L-2291A; ··· N-100.

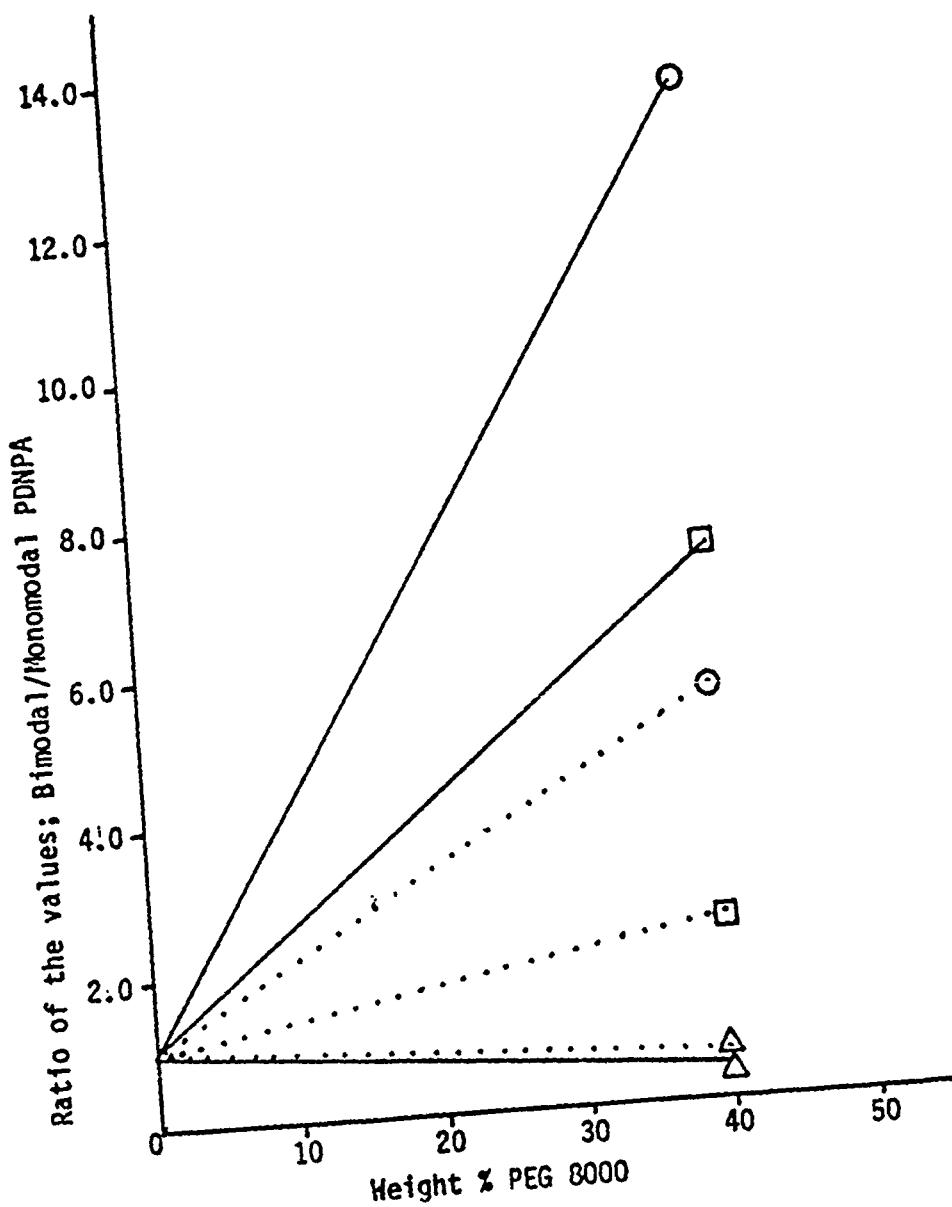
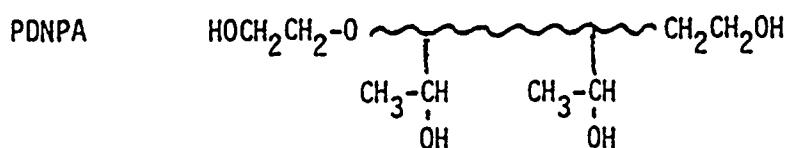
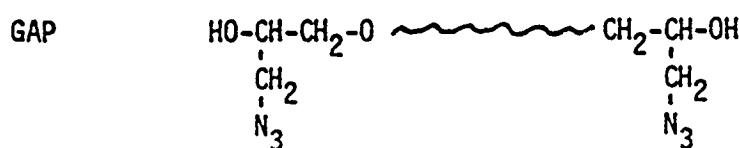


Figure 14. Reduced Stress/Strain Properties of PEG 8000/PDNPA Bimodal Systems vs. Weight % PEG 8000 at 66°C:
 (50% TEGDN; 25% 2u HMX; NCO/OH equivalent ratio = 1.2)
 Strain rate 4.2×10^{-4} m/s; $\square \sigma$; $\circ \epsilon$; $\triangle \Delta \epsilon_0$; — PTI;
 ··· M-100.

The result indicates that improvement of ultimate properties of these bimodal networks is strongly dependent on the degree of nonaffine deformation. Cross-link points created by PTI appear to allow a higher degree of nonaffine deformation than L-2291A and N-100 because they are void of urea groups and do not have components with functionality greater than three. In turn, L-2291A is superior to N-100 because it contains lower amounts of tetra- and higher functional isocyanates. This experiment clearly demonstrates that it is important to select a crosslinker which gives flexible crosslink points when an improvement of the ultimate properties is desired through a bimodal or multimodal network formation.

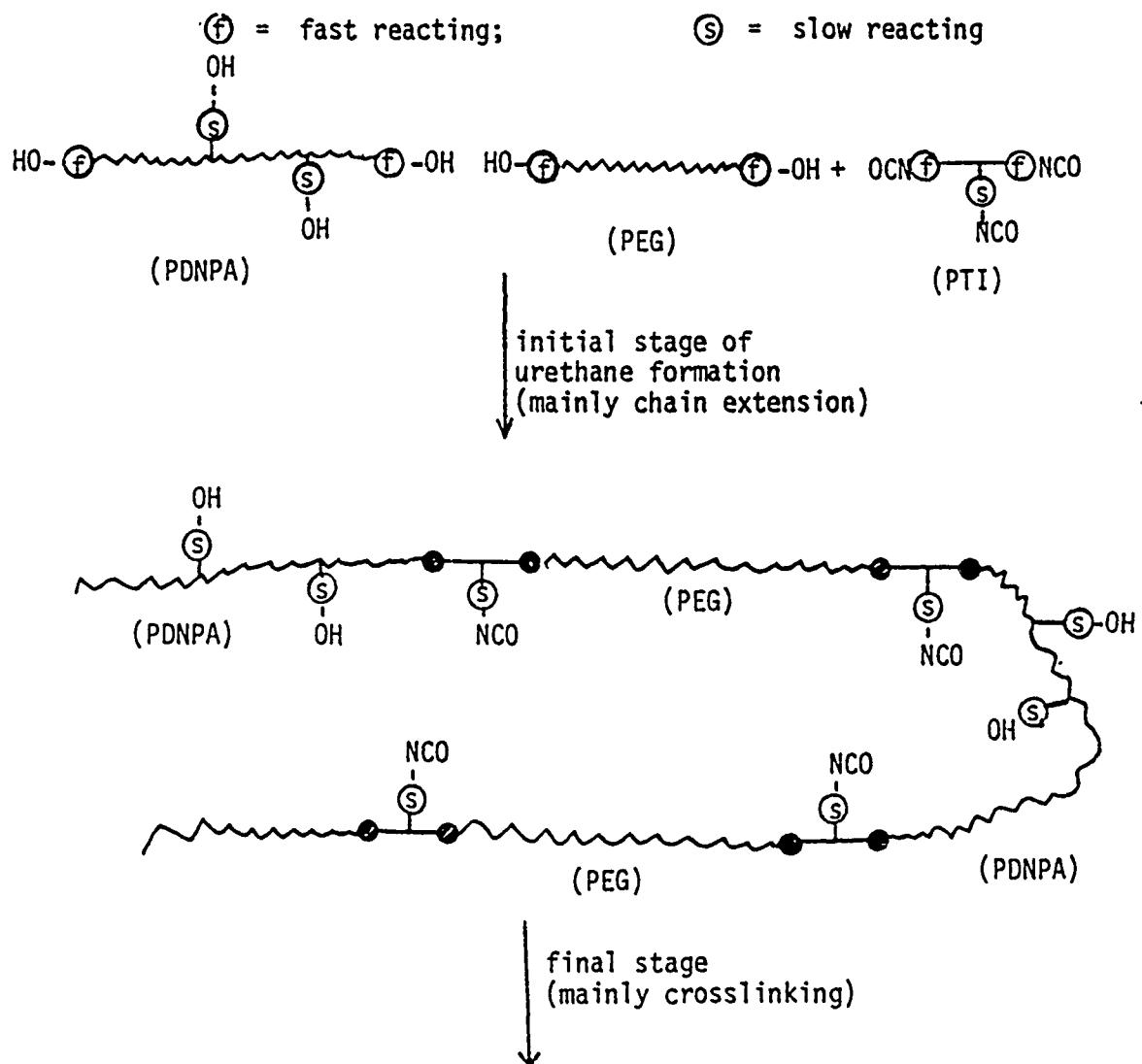
4.4 Extent of Cure Reaction (Degree of Rubber Network Formation)

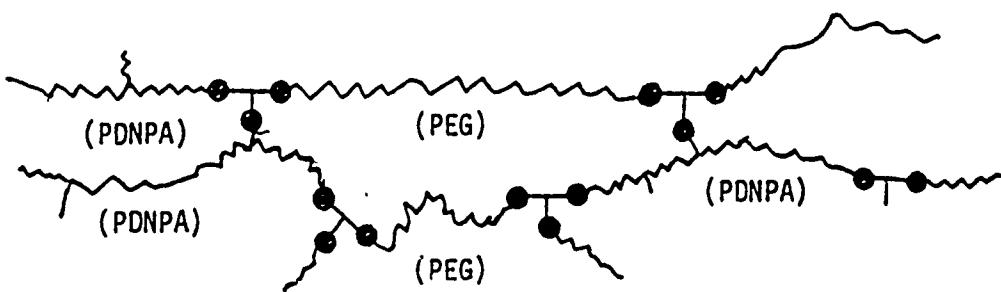
GAP from Rocketdyne contains mainly slow-reacting secondary alcohols and has a functionality of approximately two. The PDNPA used in Section 4.3 contains about 60% primary and 40% secondary alcohols and has a functionality of about four.



It has been evidenced by kinetic studies and actual binder studies that GAP does not undergo a complete cure reaction, especially when the system is highly plasticized. Competing side-reactions appear to dominate near the final stage of the urethane reaction. If urethane formation by a difunctional polymer with a triisocyanate is 98%, 94% or 92% complete, the amount of non-load bearing groups present in the rubber network can be as much as 5%, 28% or 50% respectively. On the other hand, PDNPA with the above structure would still form a complete rubber network even if some of the slow reacting secondary alcohols along the

polymeric chains fail to form urethanes with isocyanates; the fast reacting primary alcohols at the end of the chains would have already connected the polymeric chains. This is why the PDNPA/PEG 8000 bimodal systems have been so successful with PTI. The fast reacting alcohols of PEG and PDNPA react initially with the fast reacting isocyanates of PTI to create chain extension, and then the slower reacting isocyanate reacts with the secondary alcohols to create crosslink points. Hence, this system should give a minimum degree of non-load bearing chains with maximum interchain lengths as depicted below.





The use of PTI with GAP is not expected to be favorable because the slow reacting third isocyanate group of PTI and slow reacting alcohol groups of GAP tend to aggravate the incomplete urethane formation even further. This may be why the bimodal PEG 8000/GAP network cured with PTI is not superior to that with L-2291A (Figure 15). The marked difference between PEG 8000/PDNPA systems (Figure 14) and PEG 8000/GAP systems (Figure 15) leads us to believe that a complete cure reaction to create a maximum degree of load bearing chains is one of the most critical factors in achieving good mechanical properties.

4.5 Effect of Temperature

Improvements in stress/strain properties of all the polymer/PEG 8000 bimodal systems tend to be greater at 25°C than at 66°C, especially when the PEG 8000 levels exceed 40% (Figures 16, 17, 18, and 19). This may be primarily due to strain-induced crystallization of PEG 8000. Obviously, this factor outweighs the change in the viscoelastic behavior due to the lower temperature.

4.6 Effect of the Chain Length of Short Chains

Bimodal systems of PDMS (Mn 660)/(Mn 18,500) and PDMS (Mn 1100)/(Mn 18,500) used by Mark's group were compared with our PDNPA (F1)/PEG 8000 and PDNPA (M-13)/PEG 8000 systems (Figure 20). PDMS networks were neither plasticized nor filled and were tested at room temperature under near equilibrium conditions. PDNPA/PEG 8000 rubber systems contained 50 weight % triethyleneglycoldinitrate (TEGDN) and 25 weight % solid filler (2 μ HMX) and were tested at 66°C at a crosshead speed

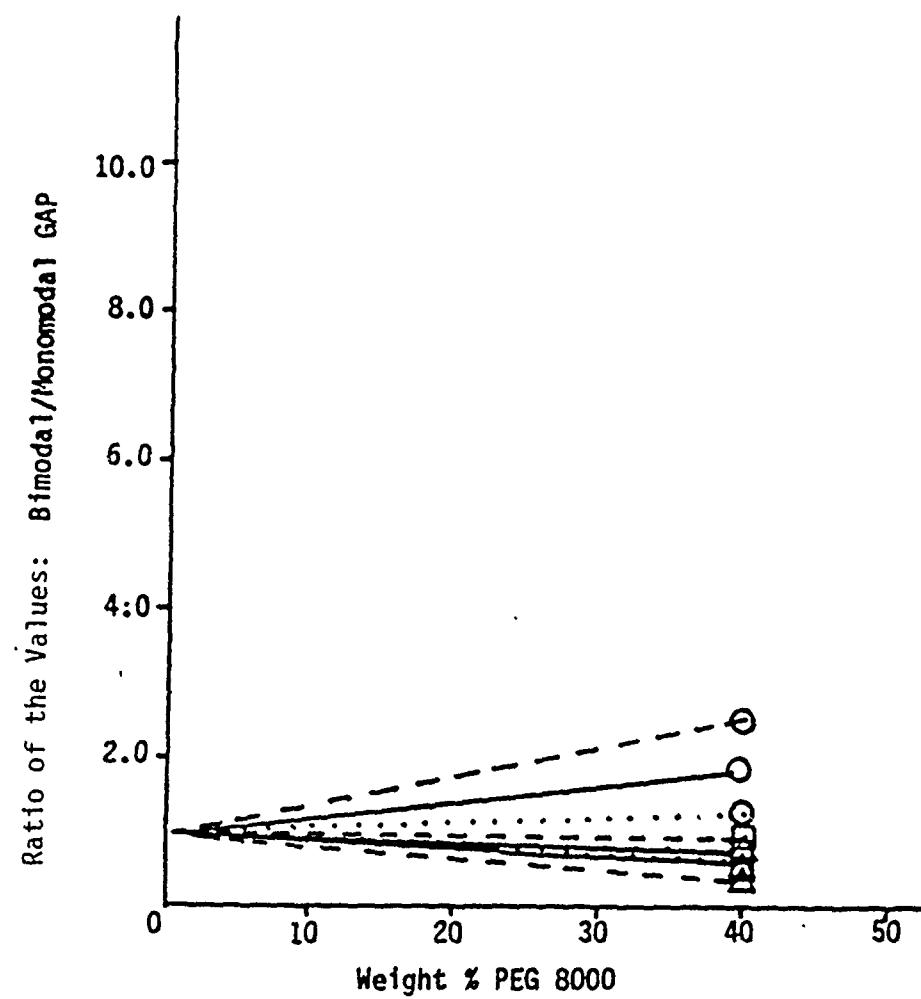


Figure 15. Reduced Stress/Strain Properties of PEG 8000/GAP Bimodal Systems vs. Weight % PEG 8000 at 66°C:
 (50% DEA; 25% 2 μ HMX; NCO/OH equivalent ratio = 1.2)
 Strain rate 4.2×10^{-4} m/s; $\square \sigma$; $\circ \epsilon$; ΔE_0 ;
 — PTI; - - - L-2291A; ····· N-100.

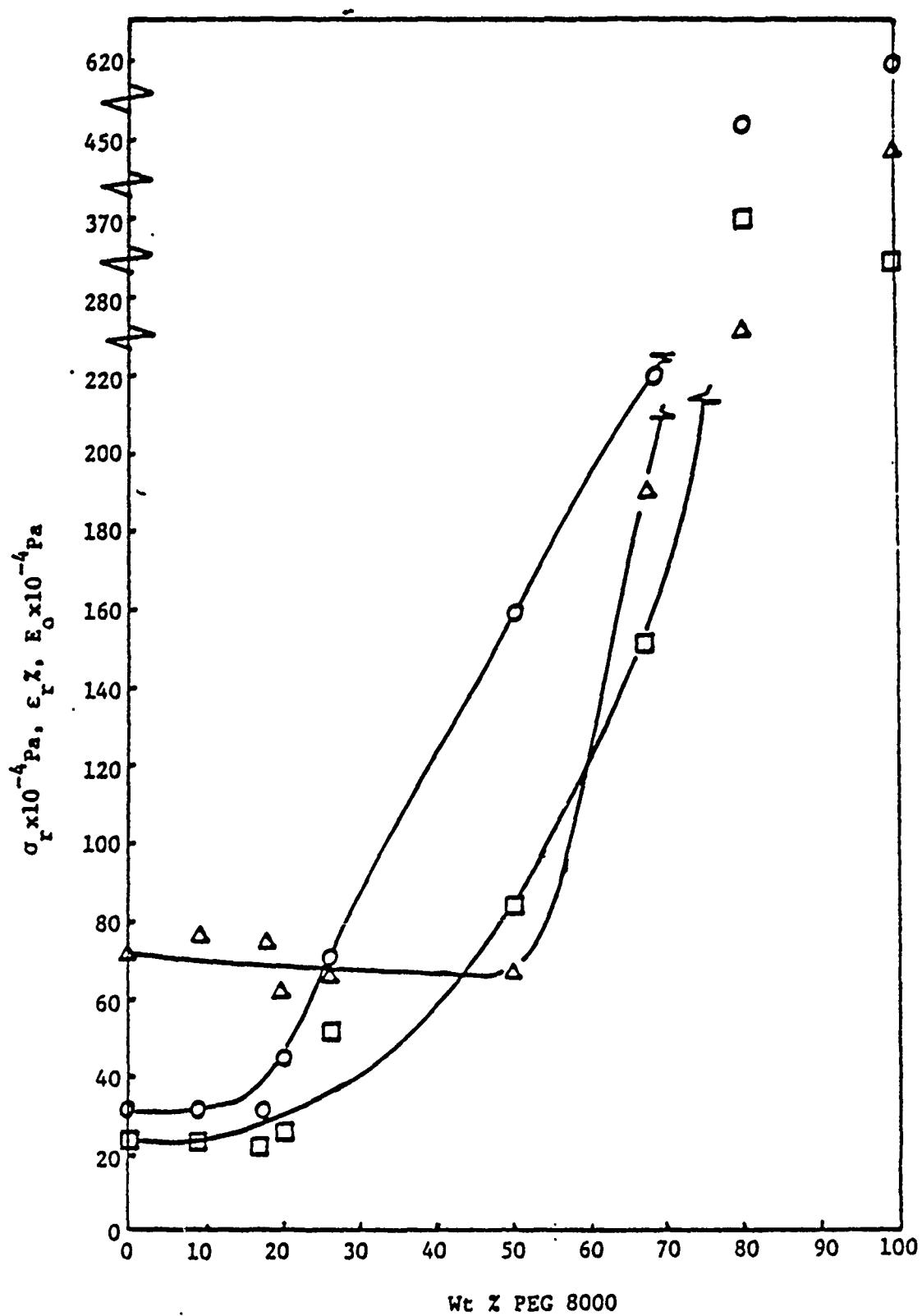


Figure 16. Ultimate Stress/Strain Properties of PDNPA (M-13)/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 25°C; Strain Rate $4.2 \times 10^{-4} \text{ m/s}$; $\square \sigma_r$; $\circ \epsilon_r$; $\triangle E_0$

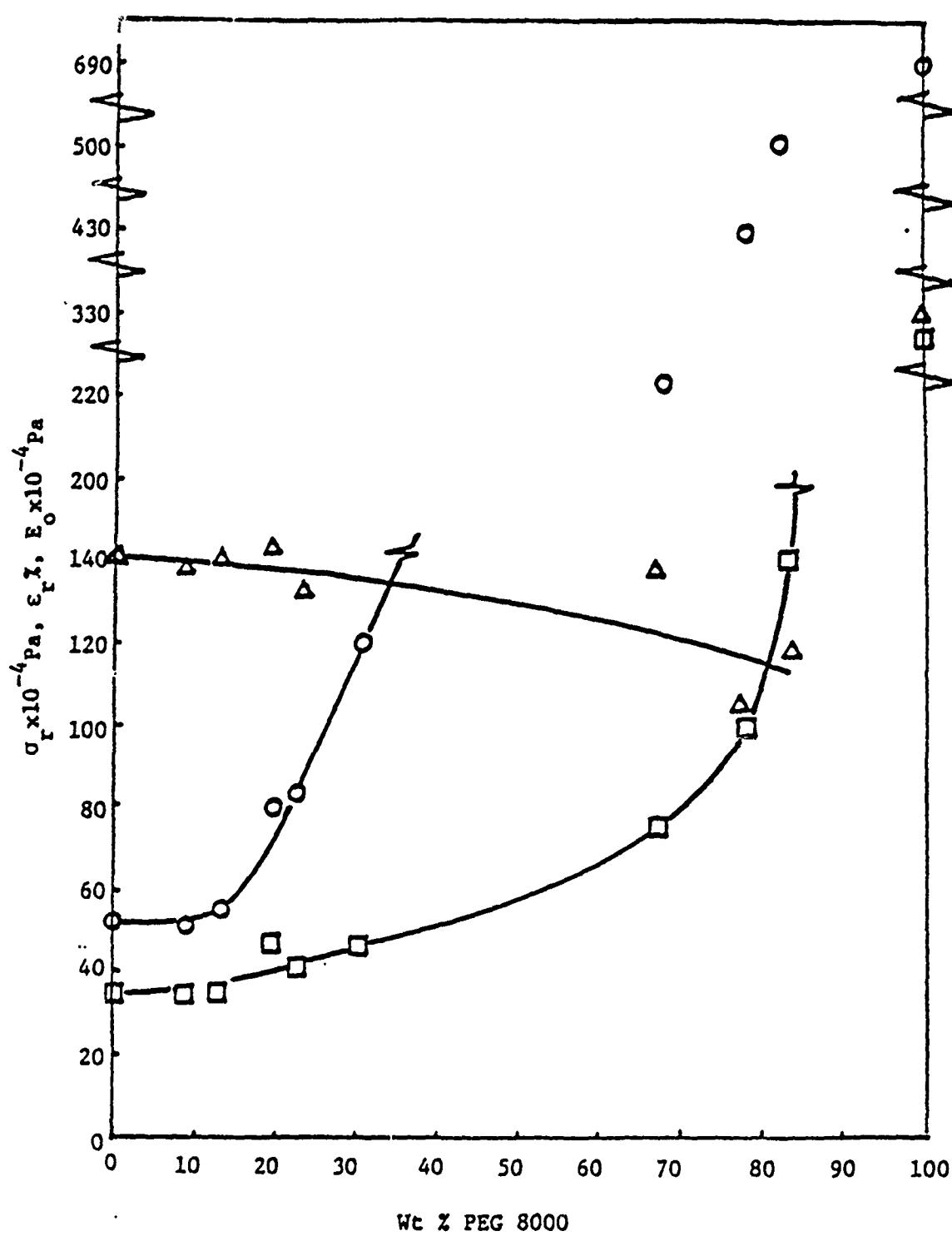


Figure 17. Ultimate Stress/Strain Properties of GAP/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 25°C; Strain Rate 4.2×10^{-4} m/s; $\square \sigma_r$; $\circ \epsilon_r$; ΔE_0

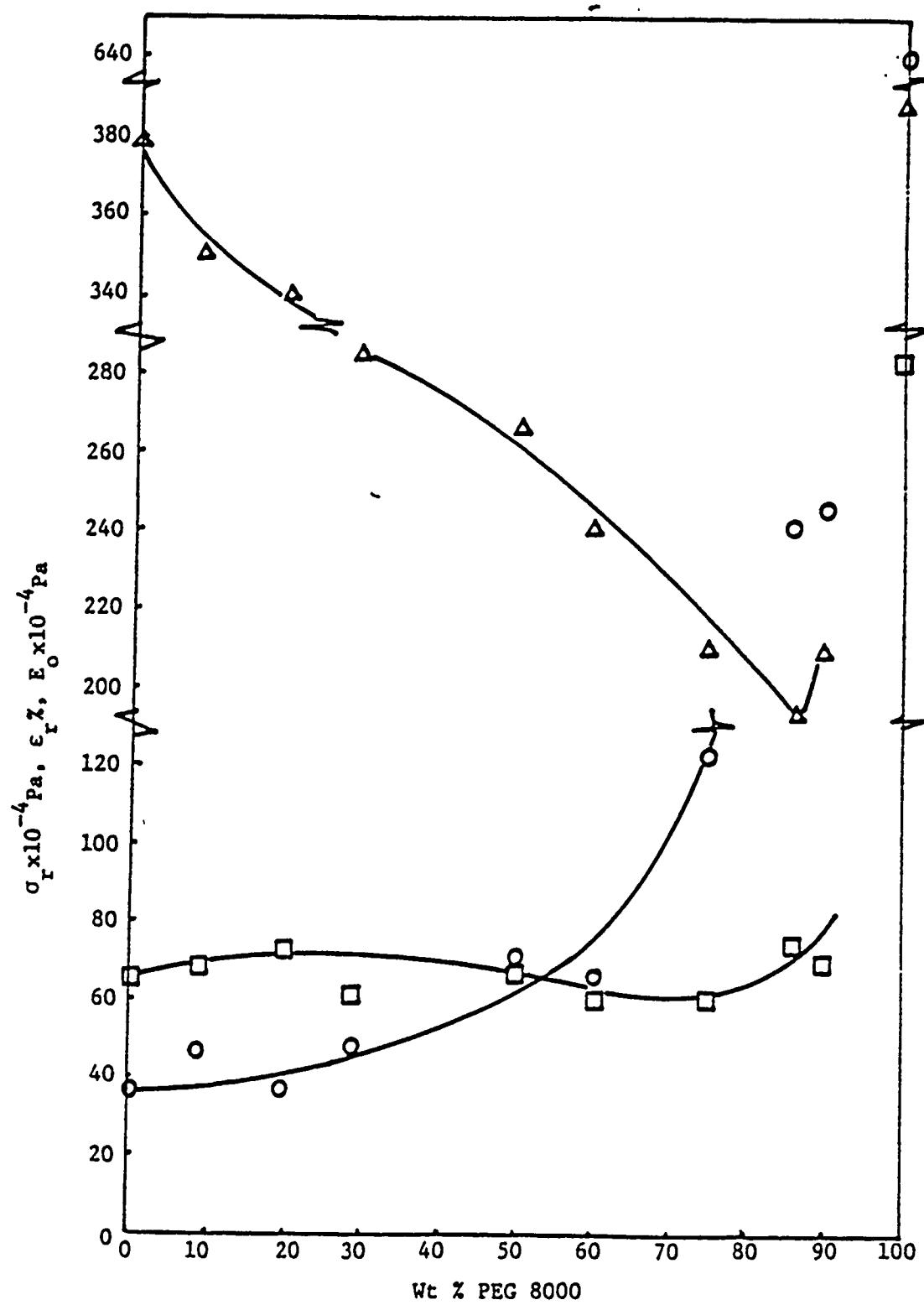


Figure 18. Ultimate Stress/Strain Properties of PEG 1000/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 25°C; Strain Rate $4.2 \times 10^{-4} \text{ m/s}$; $\square \sigma_r$, $\circ \epsilon_r$, $\triangle E_o$

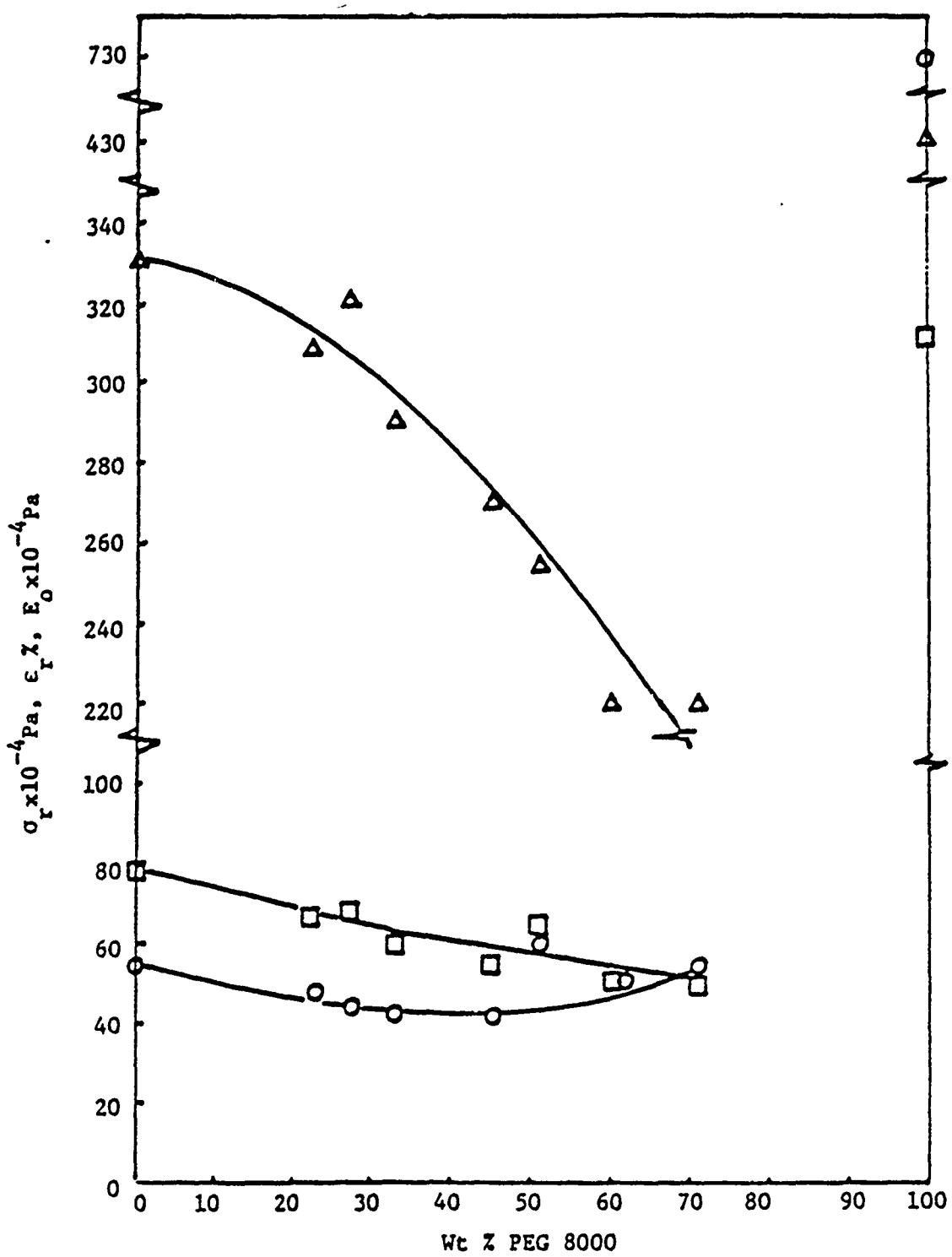


Figure 19. Ultimate Stress/Strain Properties of PEG 600/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 25°C; Strain Rate 4.2×10^{-4} m/s; $\square \sigma_r$, $\circ \epsilon_r$, $\triangle E_0$

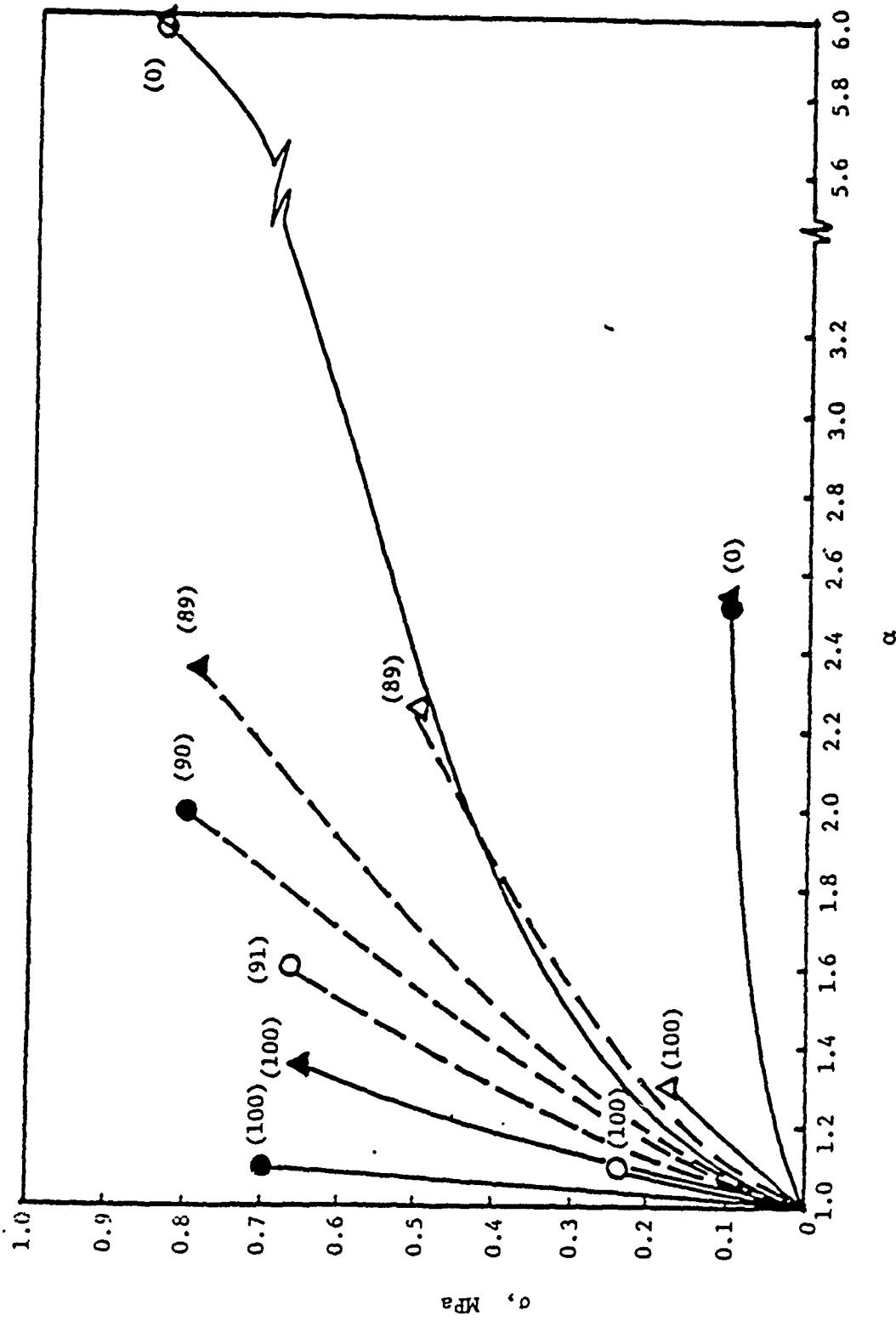


Figure 20. Stress/Strain Curves of Bimodal PDMS/PDMS and PDNPA/PEG 8000 Systems

Neat PDMS/PDMS networks were tested at 25°C under near equilibrium conditions. PDNPA/PEG 8000 networks with 50% plasticizer (TEGDN) and 25% solids (2μ HMX) were tested at 66°C at a strain rate 4.2×10^{-4} m/s. The values in () are the mole percent of short chains. ● PDMS (18 sk. atoms) or ▲ PDMS (30 sk. atoms) with long PDMS (500 sk. atoms); ○ PDNPA (20 sk. atoms) or △ PDNPA (50 sk. atoms) with PEG 8000 (550 sk. atoms); solid curves (monomodal); dotted curves (bimodal).

of 4.2×10^{-4} m/s. The long chain PDMS ($M_n = 18,500$) has an average number of skeletal atoms of 500, which is about the same length as PEG 8000 (550 skeletal atoms), since the Si-O bond length is greater than that of C-C and C-O bonds. Similarly, chain lengths of PDMS ($M_n = 660$, 18 skeletal atoms) and PDMS ($M_n = 1100$, 30 skeletal atoms) are approximately the same as those of PDNPA (F-1, 20 skeletal atoms) and PDNPA (M-13, 50 skeletal atoms).

Bimodal PDMS systems containing approximately 10 mole % of long chains show significantly greater strength capabilities than their respective short and long chain monomodal counterparts, with only a small sacrifice of the elongation capability of the long chain monomodal system (Figure 20). Hence, E_r is far greater for the bimodal systems than for the respective monomodal systems. Bimodal systems of PDNPA/PEG containing approximately 10 mole % of PEG 8000 also show significantly improved ultimate properties over the monomodal systems of PDNPA with the short chains. However, the strain of the bimodal systems is significantly inferior to that of monomodal PEG 8000, in agreement with the "weakest-link" theory. The higher ultimate stress of monomodal PEG 8000, however, is most likely due to strain induced crystallization.

At the test conditions used and with the rubbery networks studied, all the bimodal systems are in agreement with "weakest-link" theory (PDNPA/PEG systems in Figure 20 and PEG/PEG systems in Figure 9). Therefore, chain lengths of the short chains should be as long as the overall system allows, in order to achieve more favorable ultimate properties of the bimodal systems.

4.7 Effect of Chain Length vs. Mole % of PEG at a Fixed 3/7 Polymer/GAP Weight Ratio

It is desirable that the improvement of the stress/strain properties of bimodal GAP/polymer systems over monomodal GAP are achieved with a minimum amount of long chain polymer. At fixed weight fraction of a long chain polymer, one has the option of incorporating either a larger number of short polymer chains or a smaller number of long polymer chains. Stress-strain data in Table X indicate

TABLE X
 EFFECT OF 30 WEIGHT % POLYMER IN POLYMER/GAP BIMODAL SYSTEMS
 (43 Wt. % Plasticizer*1; 23 Volume % Solids)

POLYMER	POLYMER CONTENT mole %, weight %	X-Head Speed 4.2×10^{-4} m/s			
		(66°C) σ_r , MPa	ϵ_r , %	E_0 , MPa	(25°C) σ_r , MPa, ϵ_r , %, E_0 , MPa
GAP (70 sk.atms.)	100	100	0.31	43	1.4
PCP 0260 (180 sk.atms.)	100	100	0.60	95	2.0
PEG 3350 (230 sk.atms.)	100	100	0.50	100	1.5
PEG 8000 (550 sk.atms.)	100	100	0.50	380	0.8
GAP/PCP 0260	25	30	0.42	63	1.6
GAP/PEG 3350	22	30	0.43	65	1.6
GAP/PEG 8000	11	30	0.46	100	1.3

*1 Diethyleneglycoldinitrate (DEGDN)

*2 Partially crystallized.

that the incorporation of a smaller number (11 mole %) of molecules of PEG 8000 (550 skeletal atoms) is more beneficial than 22 mole % of the shorter PEG 3350 (230 skeletal atoms) or 25 mole % of shorter PCP 0260 (180 skeletal atoms). One of the reasons may be that a higher degree of strain-induced crystallization of PEG 8000 occurs compared with PEG 3350 or PCP 0260.

4.8 Effect of Solid Filler

Unfilled bimodal systems show appreciable improvements in both stress and strain properties over short chain monomodal system, whereas the solid filled systems mainly give improvement in the strain capabilities (Table XI). It is possible that the small particle filler may act as the rupture inhibitors and the improvement of stress by the filler overshadows that by nonaffine deformation.

In summary, the practical importance of the bimodal systems is clearly demonstrated in Figure 21, which shows the improved elongation of the bimodal elastomers vs. weight % of the PEG 8000. The bimodal systems of GAP and PDNPA show far greater improvement than the PEG/PEG systems at the same level of PEG 8000. For example, both PEG 600/PEG 8000 and PEG 1000/PEG 8000 systems show little improvement at 35 weight % PEG 8000, whereas GAP/PEG 8000 and PDNPA/PEG 8000 systems having short chain lengths comparable to those of the short chain PEG, show two and three-fold increases in their elongation capabilities when N-100 is used as the crosslinker. More dramatic improvement can be attained by replacing N-100 with PTI. A bimodal PDNPA F-1/PEG 8000 system cured with PTI shows an eight-fold increase at the same PEG 8000 level, in spite of the fact that it has the shortest chain length (20 skeletal atoms).

One would desire a maximum improvement with minimum incorporation of the long chain polymer, i.e. less dilution of other favorable properties of the short chain polymers, such as low viscosity and energy level. The most important factor in these systems appears to be the type of crosslinker. Flexible crosslink

TABLE XI
EFFECT OF SOLIDS ON GAP/PEG BIMODAL SYSTEMS
(6/4 - Plasticizer/Polymer weight ratio)

GAP/PEG 8000 (wt.% PEG)	Volume % Solids	X-head Speed 4.2×10^{-4} m/s at 66°C		
		σ_r , MPa	ϵ_r , %	E_0 , MPa
0	0	0.07	18	0.6
30	0	0.24	80	0.9
0	23	0.31	43	1.4
30	23	0.46	100	1.3
0	40	0.35	48	1.6
30	40	0.42	95	1.5

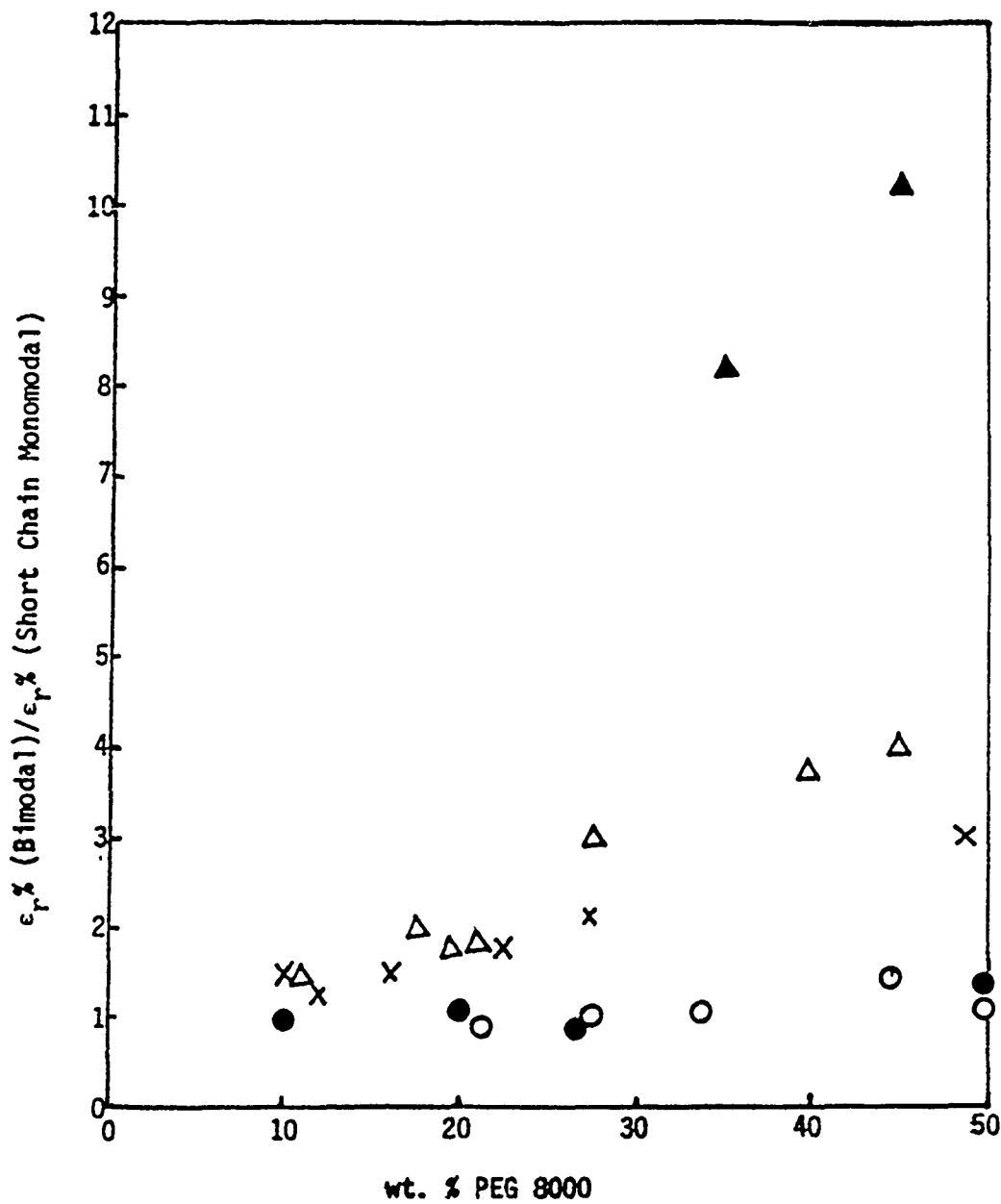


Figure 21. Improvement of Ultimate Strain Properties of Various Polymer/PEG 8000 Bimodal Systems vs Wt % PEG 8000 at 66°C; Strain Rate 4.2×10^{-4} m/s; Composite: 24% polymer, 50% TEGDN, 25% HMX; ○ PEG 600; ● PEG 1000; X GAP; Δ PDNPA M13; ▲ PDNPA F-1. (PDNPA F-1 was cured with PTI. The rest were cured with N-100)

points allow more extensive nonaffine deformation, thus improving the ultimate strain further.

5.0 EXPERIMENTAL

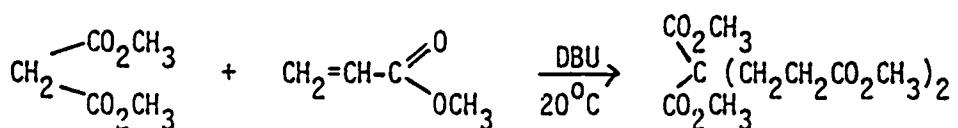
5.1 Chemicals and Polymers

5.1.1 Prepolymers

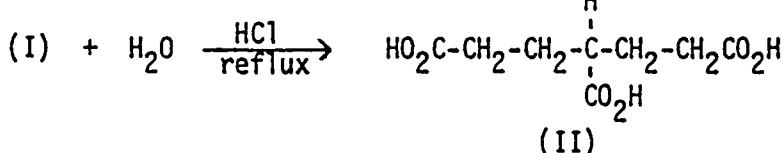
GAP was synthesized by Rocketdyne and the procedure was reported. Linear hydroxy-terminated polybutadiene was custom synthesized by Phillips. R-45M was purchased from Arco. PDNPA was synthesized and characterized as described in the previous report.⁶ Various molecular weight PEG and PCP0260 were purchased from Union Carbide.

5.1.2 Isocyanates

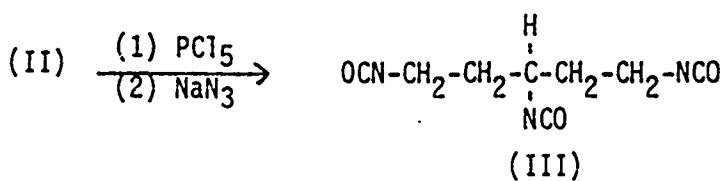
Desmodur N-100 and L-2291A were obtained from Mobay Chemical Company. They are mixtures of isocyanates with average functionalities greater than 3 according to the GPC analysis of the isocyanates and their n-octanol derivatives(Figures 3 and 4). PTI is a new trifunctional isocyanate specifically synthesized for this project. The reaction for the synthesis involves:



(I)



(II)

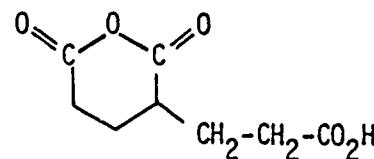


(III)

5.1.2.1 Synthesis of Pentane-1,3,5-tricarboxylic acid (II)

Dimethyl malonate (66 g, .5 mole) was combined with diazobicycloundecene (DBU) (2.0 g). This mixture was cooled by means of a water bath, and methyl acrylate (150 ml) was added carefully, over 2 hours, keeping the reaction mixture below 50⁰C at all times. After the addition was complete, the reaction mixture was left at room temperature for 2 days, freed of volatiles in vacuo, and allowed to solidify into a clear, crystalline mass, 156 g of (I) (100%). ¹H nmr (CCl₄) (Figure 22), mp 51-55⁰C.

The 156 g of solid derived from the DBU-catalyzed Michael addition of malonic ester to acrylate ester was then dissolved in 500 ml of 36% aqueous HCl, diluted to 1 liter, and refluxed vigorously for 4 days. The water and HCl were then distilled off at atmospheric pressure until the entire volume of the reaction mixture had reached approximately 150 ml. At this time, the viscous residue was allowed to crystallize, giving 60 g (60%) of crystals, mp 102-104⁰. This melting point was found to concur with that of octric anhydride with the structure below. Evidently, the acid and the anhydride are in equilibrium under the acidic conditions of the reaction.



5.1.2.2 Conversion of Octric Anhydride to 1,3,5-triisocyanatopentane (III)

The octric anhydride (5 g, .025 mole) was suspended in thionyl chloride (25 ml) and refluxed vigorously for 36 hours, at which point the insoluble crystals dissolved completely. Next, phosphorous pentachloride (5 g, .025 mole) was added in order to convert any unreacted anhydride over to acid chloride; this mixture was stirred for 15 hours. To destroy excess phosphorous pentachloride, acetic anhydride (4 ml) was added, an exotherm was observed, and,

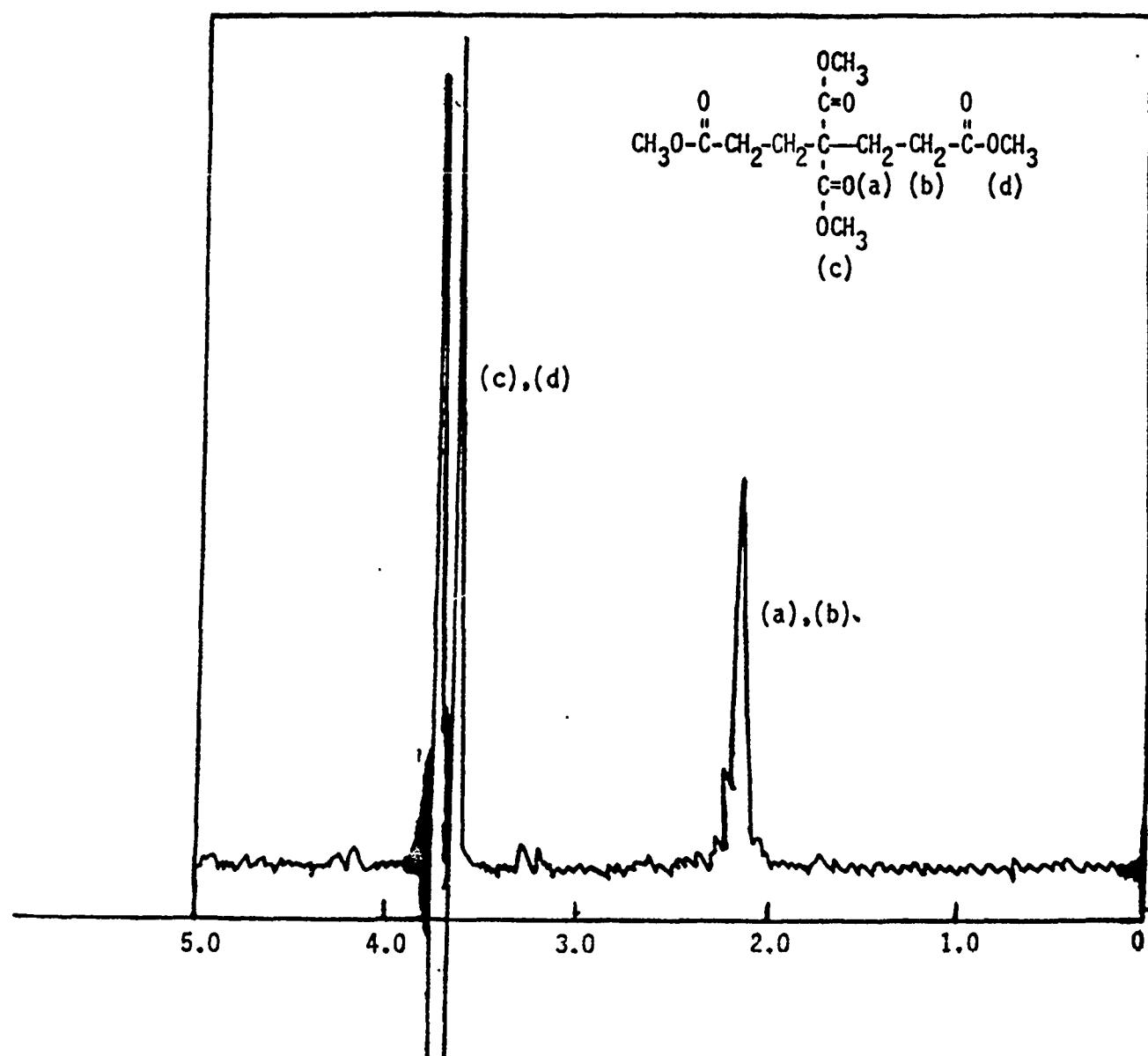


Figure 22. ^1H NMR in CCl_4

finally, all volatile materials were removed under high vacuum in preparation for the Curtius reaction. The crude 1,3,5-tris-(chlorocarbonyl) pentane was not purified, as it was neither crystalline nor distillable.

A mixture of 10 g NaN_3 , 35 ml CHCl_3 , and 25 ml of water was stirred vigorously at 0°C . The entire quantity of the triacid chloride was added to this mixture. This mixture was stirred for 1 hour at 0°C , at which time an infrared spectrum of a small aliquot revealed the presence of unreacted acid chloride (1760 cm^{-1}) along with acid azide (1700 cm^{-1} , 2150 cm^{-1}).

To accelerate the reaction, 20 ml of acetone was then added; the reaction was worked up after stirring for a second hour. No acid chloride remained. The reaction mixture was combined with 200 ml ether, and washed with 100 ml of 1M Na_2CO_3 , and dried over MgSO_4 . Next, the ether was removed in vacuo and replaced with 200 ml of toluene, half of which was evaporated in vacuo to remove traces of water. Care was taken not to concentrate the acid azide to a volume of less than 15 ml, as the neat material would pose a serious explosion hazard.

The solution of acid azide in toluene was heated to 100°C for 30 min., at which time gas evolution from the resulting Curtius rearrangement had ceased. The reaction was treated with decolorizing charcoal, and the toluene was removed in vacuo. The residue was distilled under high vacuum, giving 2.5 g (50%) of the desired product (III), a heavy oil, bp 140°C , 1 mm Hg.

^1H nmr (CCl_4): δ 1.5-1.9: multiplet, integration = 4; δ 3.5: triplet, $j = 6\text{Hz}$, integration = 4; δ 3.6-4.0: multiplet, integration = 1 (Figure 23); IR: 2260 cm^{-1} (Figure 24). Elemental analysis: %C 49.12; %H 4.65; %N 21.71 (Theoretical: %C 49.23; %H 4.61; %N 21.54).

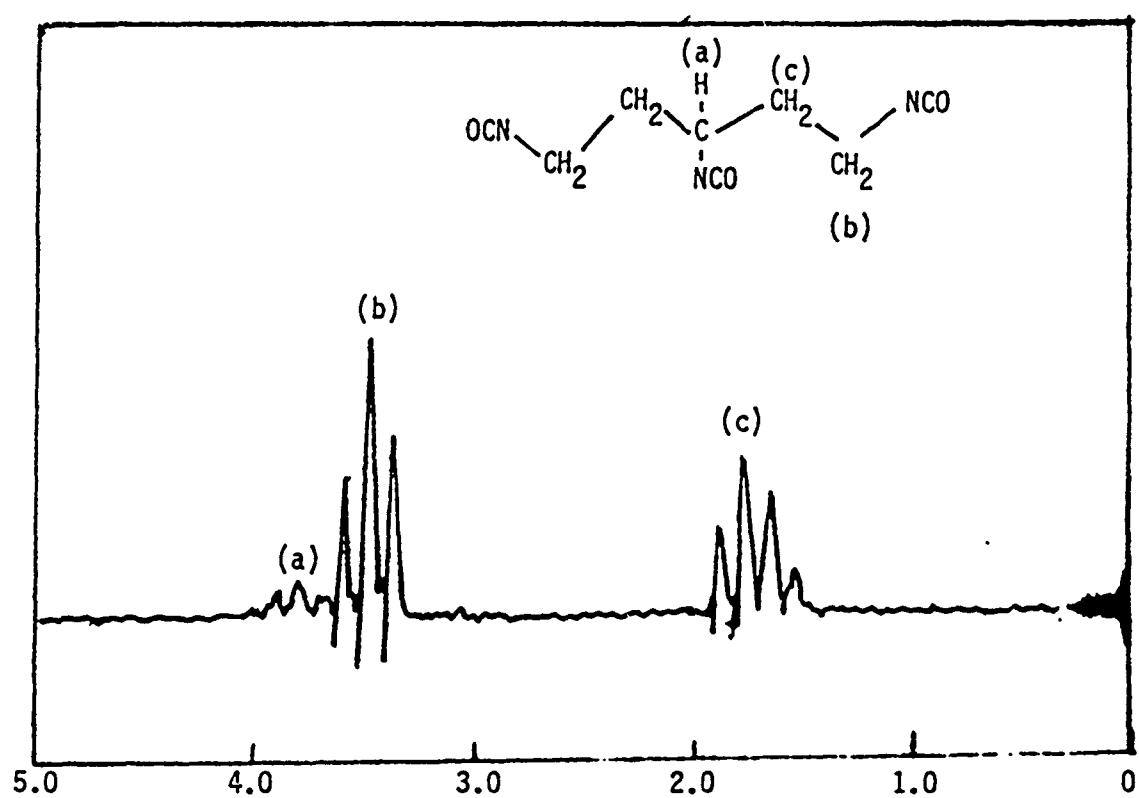


Figure 23. ^1H NMR in CCl_4

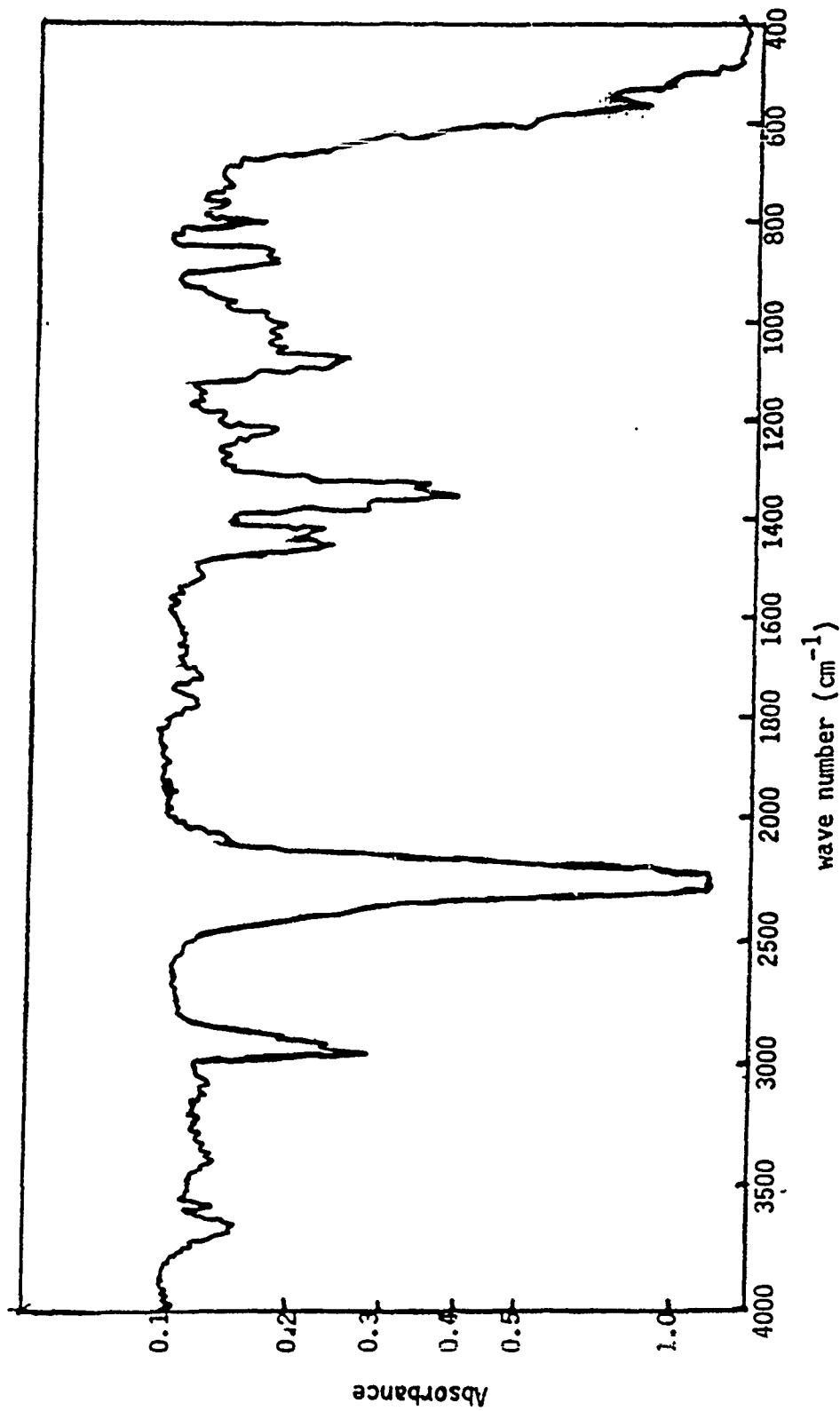


Figure 24. IR of PTI (neat)

5.2 Preparation of Rubber Samples

Prepolymers, predissolved in plasticizer and the other ingredients of the composite such as isocyanate, solid filler, and catalyst were mixed thoroughly while degassing under vacuum and then cast on a plate. The samples were cured for two days at 45⁰C. A longer cure time did not change the swelling ratio of the rubber, indicating that the cure reaction was as complete as possible under the conditions.

5.3 Stress/Strain Properties

The cast samples, approximately 3×10^{-3} m thick, were stamped out using the cutting die shown in Figure 25. Tensile properties of these minibone specimens were tested according to ASTM C1708-79. The properties obtained were nominal stress, (σ), percent elongation (ϵ) or extension ratio (α), and initial modulus (E_0).

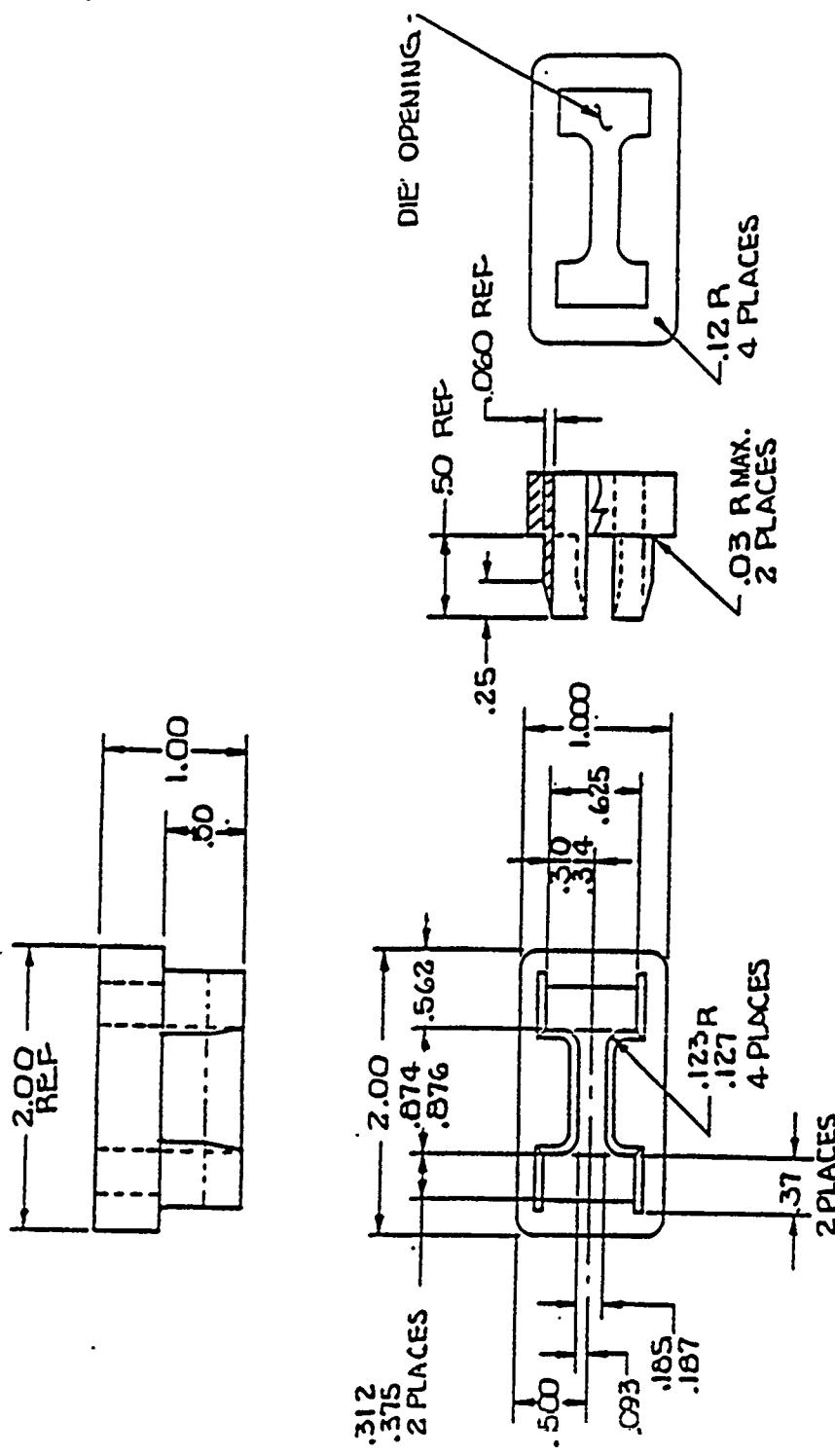


Figure 25. Dimensions of Cutting Die, Full Scale

6.0 REFERENCES

1. R.J. Young, "Introduction to Polymers", pp 245-256, Chapman and Hall (1981).
2. A.E. Oberth, Rubber Chem. and Technology, 44, No. 1, 152-165 (1971).
3. A.L. Andrade, M.A. Llorente, M.A. Sharaf, R.R. Rahalkar and J.E. Mark, J. of Applied Poly:Sci. 26, 1829-1836 (1981).
4. M.A. Llorente, A.L. Andrade, and J.E. Mark, J. Poly. Sci. Poly. Phys. Ed. 19, 621-630 (1981).
5. F. Bueche, "Physical Properties of Polymers," Interscience, New York (1962).
6. A.L. Andrade, M.A. Llorente, and J.E. Mark, J. Chem. Phys. 72, 2282 (1980).
7. C.S. Youn Kim, A.L. Dodge, S.F. Lau and A. Kawasaki, Anal. Chem. 54, 232-238 (1982).
8. C.S. Youn Kim, "Synthesis of Hydroxy-Terminated Dinitropropyl Acrylate Polymers and Improved Characterization of Hydroxy-Terminated Prepolymers," AFRPL TR-83-002 (1983).